

# United States Patent [19]

Takahashi et al.

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[54] **FUNGICIDAL ANILINE DERIVATIVES**

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[63] Continuation-in-part of Ser. No. 485,295, Apr. 15,  
1983.

[30] **Foreign Application Priority Data**

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[51] Int. Cl.<sup>4</sup> ..... **A01N 47/20; C07C 125/065**

[52] U.S. Cl. .... **514/485; 560/29**

[58] Field of Search ..... 560/24, 29; 424/300;  
260/465 D, 455 A; 514/485

[56] **References Cited**

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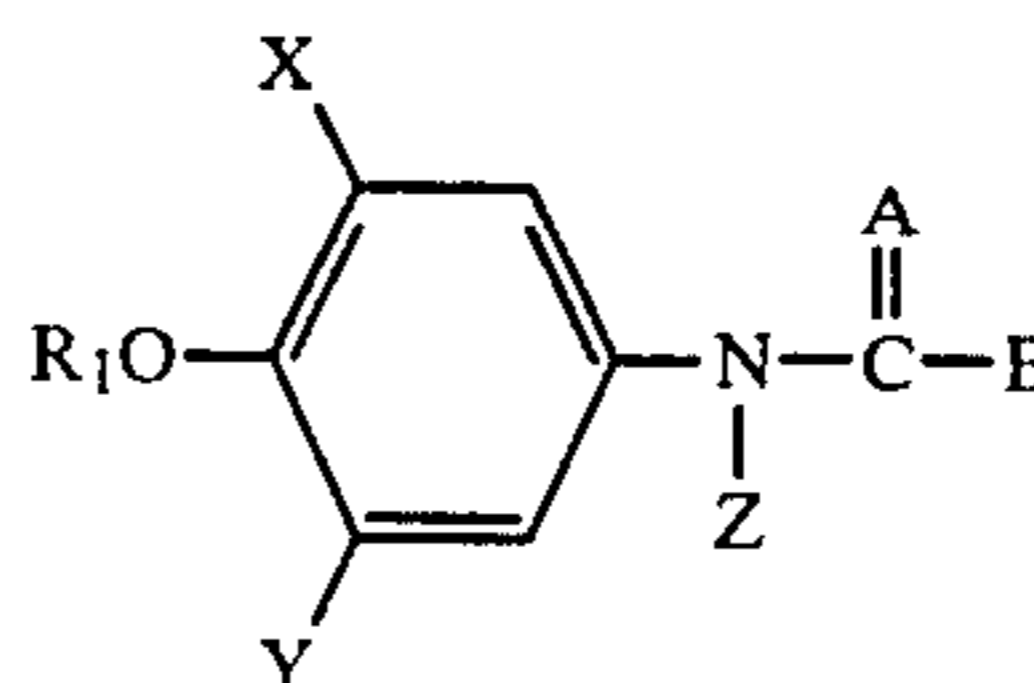
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[57] **ABSTRACT**

A compound of the formula:



useful as a fungicidal agent against phytopathogenic  
fungi, and particularly against strains resistant to benz-  
imidazole, thiophanate and/or cyclic imide fungicides.

**5 Claims, No Drawings**

## FUNGICIDAL ANILINE DERIVATIVES

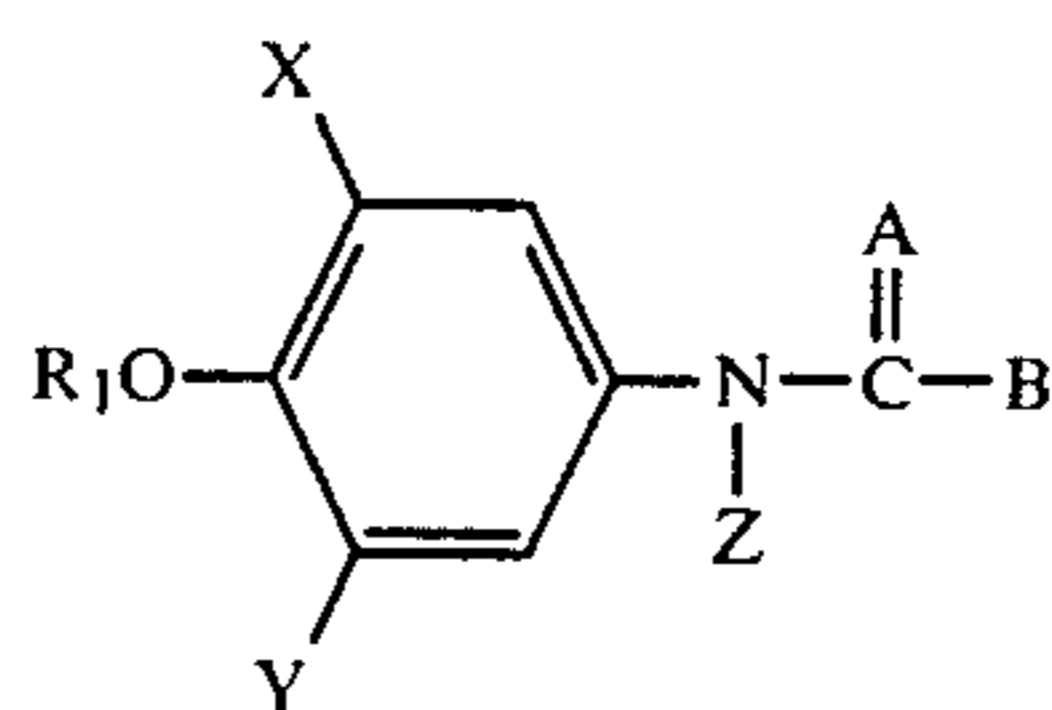
This is a continuation-in-part application of our co-pending application Ser. No. 485,295 filed on Apr. 15, 1983.

This invention relates to fungicidal aniline derivatives.

Benzimidazole and thiophanate fungicides such as Benomyl (methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate), Fubelidazol (2-(2-furyl)benzimidazole), Thiabendazole (2-(4-thiazolyl)benzimidazole), Carben-dazim (methyl benzimidazol-2-ylcarbamate), Thiopha-nate-methyl (1,2-bis(3-methoxycarbonyl-2-thioureido)-benzene), Thiophanate (1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene), 2-(O,S-dimethylphosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene and 2-(O,O-dimethylthiophosphorylamino)-1-(3'-methox-ycarbonyl-2'-thioureido)benzene are known to show an excellent fungicidal activity against various plant patho-genic fungi, and they have been widely used as agricul-tural fungicides since 1970. However, their continuous application over a long period of time provides phyto-pathogenic fungi with tolerance to them, whereby their plant disease-preventive effect is much lowered. Fur-ther, the fungi which gained tolerance to certain kinds of benzimidazole or thiophanate fungicides also show considerable tolerance to some other kinds of benzimid-azole or thiophanate fungicides. Thus, they are apt to obtain cross-tolerance. Therefore, if any material de-crease of their plant disease-preventive effect in certain fields is observed, their application to such fields has to be discontinued. But, it is often observed that the den-sity of drug-resistant organisms is not decreased even long after the discontinuation of the application. Al-though other kinds of fungicides have to be employed in such case, only few are so effective as benzimidazole or thiophanate fungicides in controlling various phyto-pathogenic fungi. Cyclic imide fungicides such as Procymidone (3-(3', 5'-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide), Iprodione (3-(3', 5'-dichlorophenyl)-1-isopropylcarbamoylimidazolidine-2,4-dione), Vinchlozolin (3-(3', 5'-(dichlorophenyl)-5-methyl-5-vinylloxazolidine-2,4-dione), ethyl (RS)-3-(3', 5'-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate, etc., which are effective against various plant diseases, particularly those caused by *Botrytis cinerea*, have the same defects as previously explained with respect to the benzimidazole and thiophanate fun-gicides.

In C.R. Acad. Sc. Paris, t. 289, S'erie D, pages 691-693 (1979), it is described that such herbicides as Barban (4-chloro-2-butynyl N-(3-chlorophenyl)carbamate), Chlorobufam (1-methyl-2-propynyl N-(3-chloro-phenyl)carbamate), Chlorpropham (isopropyl N-(3-chlorophenyl)carbamate) and Propham (isopropyl N-phenylcarbamate) exhibit a fungicidal activity against certain organisms tolerant to some of the benzimidazole or thiophanate fungicides. However, their fungicidal activity against the drug-resistant fungi is not strong enough, and hence, practically they can not be used as fungicides.

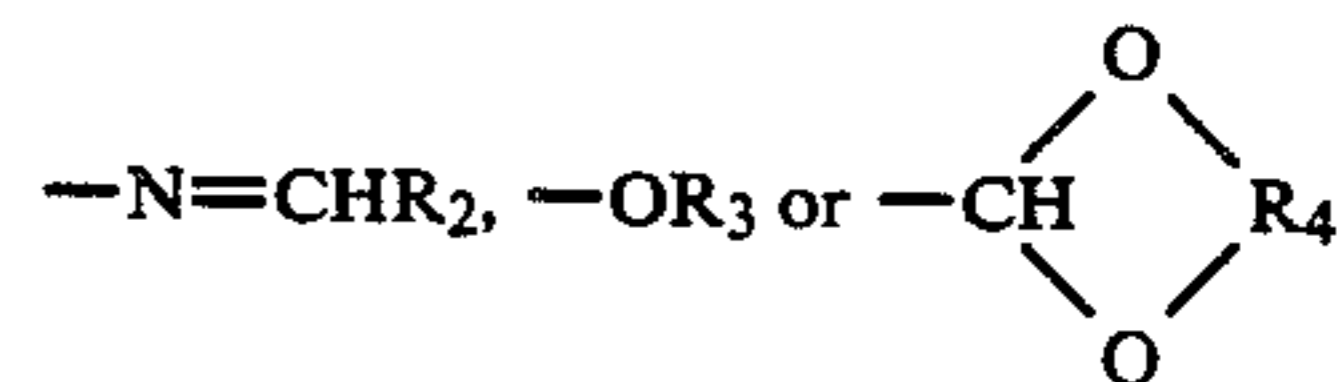
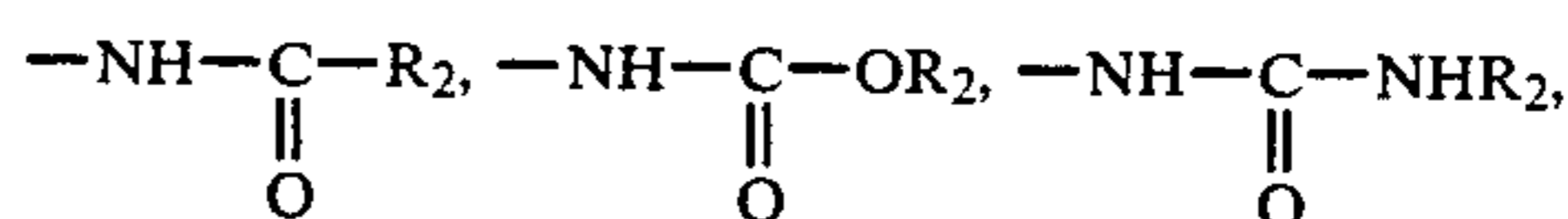
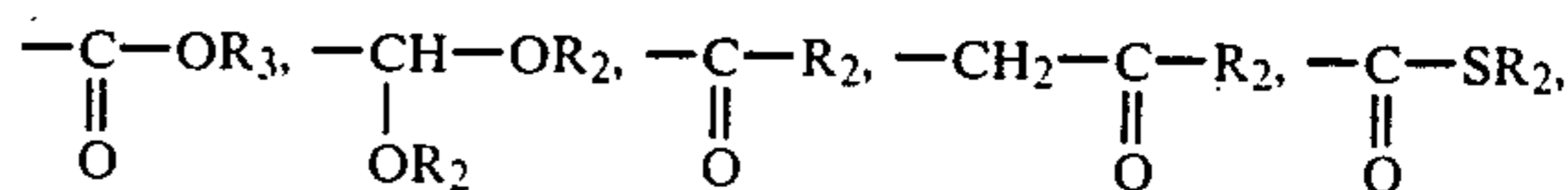
As a result of a study seeking a new type of fungi-cides, it has now been found that aniline derivatives of the formula:



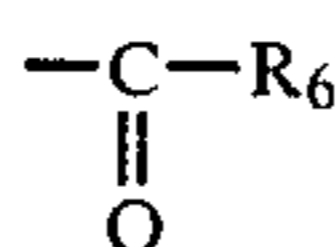
(I)

wherein X and Y are, the same or different, each a hydrogen

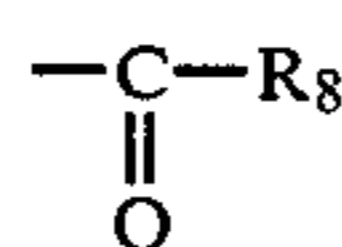
a halogen atom, a lower alkyl group, a halo(lower)-alkyl group, a lower alkenyl group, a lower alkynyl group, a cyano group, a hydroxyiminomethyl group, a lower alkoxy-iminomethyl group or a group of the formula:  $-\text{CH}_2\text{OR}_2$ ,



in which  $\text{R}_2$  is a lower alkyl group,  $\text{R}_3$  is a lower alkyl group, a lower alkenyl group or a lower alkynyl group and  $\text{R}_4$  is a lower alkylene group, with the proviso that when either one of X and Y is a hydrogen atom, the other is not a hydrogen atom;  $\text{R}_1$  is a halo(lower)alkenyl group, a halo(lower)alkynyl group, a cyano group, a hydroxy(lower)alkyl group, a lower alkoxy(lower)alke-nyl group, a lower alkoxy(lower)alkynyl group, a cyano(lower)alkyl group or a group of the formula:  $-\text{CH}_2\text{R}_5$ ,



or  $-\text{SO}_2\text{R}_7$  in which  $\text{R}_5$  is a lower alkoxy-carbonyl group, an acyl group (e.g. lower alkanoyl, benzoyl) or a lower alkylthio group,  $\text{R}_6$  is a lower alkyl group, a lower alkoxy group or a lower alkylamino group and  $\text{R}_7$  is a lower alkyl group, a halo(lower)alkyl group or a lower alkylamino group; Z is a hydrogen atom, a hy-droxyl group, a lower alkoxy group, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a lower alkoxy-carbonyl-(lower) alkyl group, a lower alkoxy-carbonyloxy group, a lower alkyl-carbonyloxy group or a group of the formula:



or  $-\text{SR}_9$  in which  $\text{R}_8$  is a lower alkyl group, a cyclo(-lower)-alkyl group, a halo(lower)alkyl group, a lower alkoxyalkyl group or a phenyl group and  $\text{R}_9$  is a lower alkyl group, a lower alkoxy-carbonyl group or a phenyl group; A is an oxygen atom or a sulfur atom; and B is a lower alkyl group, a lower alkenyl group, a cyclo(low-er)alkyl group, a phenyl group or a group of the for-mula:  $-\text{W}-\text{R}_{10}$  in which W is an oxygen atom or a sulfur

atom and R<sub>10</sub> is a cyclo(lower)alkyl group, a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a halo(lower)alkenyl group, a halo(lower)alkynyl group, a phenyl group, a phenyl group substituted with a halogen atom, a cyclo(lower)alkyl(lower)alkyl group or a lower alkyl group substituted with a member selected from the group consisting of halogen, cyano, lower alkoxy, phenyl, lower alkenyloxy, halo(lower)alkoxy, phenoxy and ar(lower)alkoxy (e.g. phenyl(lower)alkoxy), show an excellent fungicidal activity against plant pathogenic fungi which have developed resistance to benzimidazole, thiophanate and/or cyclic imide fungicides. It is notable that their fungicidal potency against the organisms tolerant to benzimidazole, thiophanate and/or cyclic imide fungicides (hereinafter referred to as "drug-resistant fungi" or "drug-resistant strains") is much higher than that against the organisms sensitive to benzimidazole, thiophanate and/or cyclic imide fungicides (hereinafter referred to as "drug-sensitive fungi" or "drug-sensitive strains").

The term "lower" used hereinabove and hereinafter in connection with alkyl, alkenyl, alkynyl, alkylene, alkoxy, etc. is intended to have not more than 6 carbon atoms.

Among the compounds of the formula (I), 3,5-dichloro-4-cyanooxymethacrylanilide and 3-methyl-4-cyanooxymethacrylanilide (Belgian Pat. No. 670,675) and 2-chloro-4-acetylamino-6-methylphenyl N-methylcarbamate (Nippon Oyo Dobutsu Konchu Gakkai-Shi (Journal of Japanese Applied Animal and Insecticidal Research Organization), 12 (4), 202-210 (1968)) are known. However, it has not been known or reported that they have any fungicidal activity or are useful as fungicides.

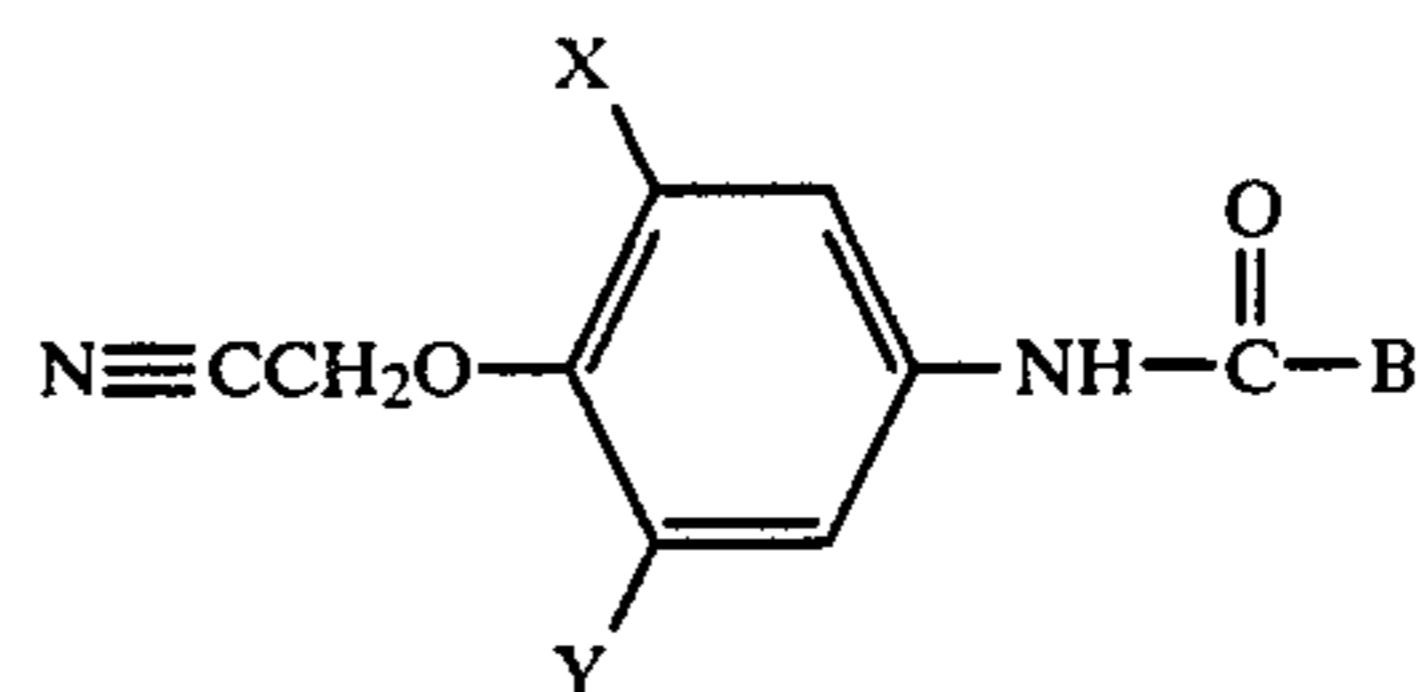
The compounds (I) are fungicidally effective against a wide scope of plant pathogenic fungi, of which examples are as follows: *Podosphaera leucotricha*, *Venturia inaequalis*, *Mycosphaerella pomi*, *Marssonina mali* and *Sclerotinia mali* of apple, *Phyllactinia kalicola* and *Gloeosporium kaki* of persimmon, *Cladosporium carpophilum* and *Phomopsis* sp. of peach, *Cercospora viticola*, *Uncinula necator*, *Elsinoe ampelina* and *Glomerella cingulata* of grape, *Cercospora beticola* of sugarbeet, *Cercospora arachidicola* and *Cercospora personata* of peanut, *Erysiphe graminis* f. sp. *hordei*, *Cercospora herpotrichoides* and *Fusarium nivale* of barley, *Erysiphe graminis* f. sp. *tritici* of wheat, *Sphaerotheca fuliginea* and *Cladosporium cucumerinum* of cucumber, *Cladosporium fulvum* of tomato, *Corynespora melongenae* of eggplant, *Sphaerotheca humuli*, *Fusarium oxysporum* f. sp. *fragariae* of strawberry, *Botrytis alli* of onion, *Cercospora apii* of celery, *Phaeoisariopsis griseola* of kidney bean, *Erysiphe cichoracearum* of tobacco, *Diplocarpon rosae* of rose, *Elsinoe fawcetti*, *Penicillium italicum*, *Penicillium digitatum* of orange, *Botrytis cinerea* of cucumber, eggplant, tomato, strawberry, pimiento, onion, lettuce, grape, orange, cyclamen, rose or hop, *Sclerotinia sclerotiorum* of cucumber, eggplant, pimiento, lettuce, celery, kidney bean, soybean, azuki bean, potato or sunflower, *Sclerotinia cinerea* of peach or cherry, *Mycosphaerella melonis* of cucumber or melon, etc. Namely, the compounds (I) are highly effective in controlling the drug-resistant strains of said fungi.

The compounds (I) are also fungicidally effective against fungi sensitive to said known fungicides as well as fungi to which said known fungicides are ineffective. Examples of such fungi are *Pyricularia oryzae*,

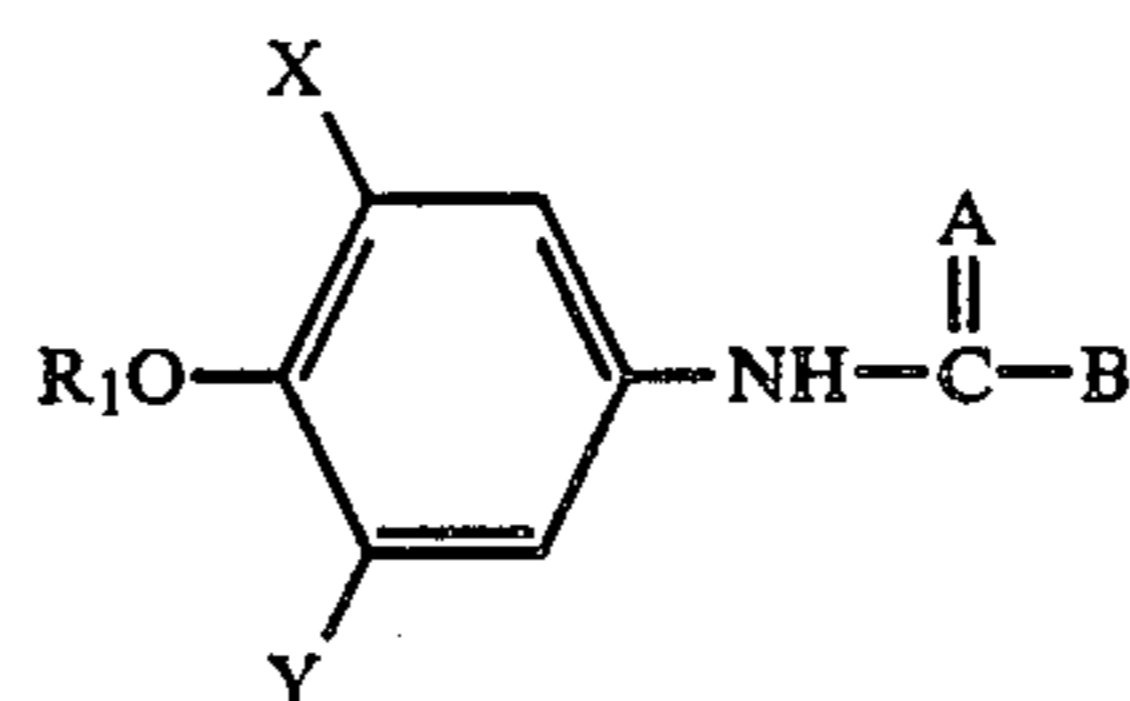
*Pseudoperonospora cubensis*, *Plasmopara viticola*, *Phytophthora infestans*, etc.

Advantageously, the compounds (I) are of low toxicity and have little detrimental actions on mammals, fishes and so on. Also, they may be applied to the agricultural field without causing any material toxicity to important crop plants.

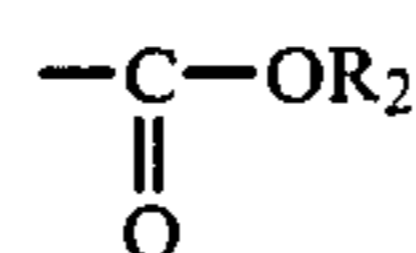
In view of their excellent fungicidal properties, particularly useful is a compound of the formula:



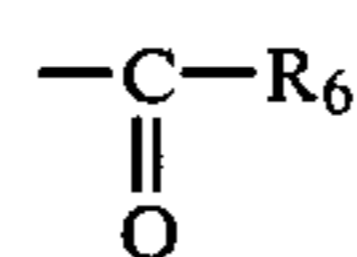
wherein X, Y and B are each as defined above, or a compound of the formula:



wherein X and Y are, the same or different, each a hydrogen atom, a halogen atom, a lower alkyl group, a lower alkoxy group or a group of the formula: —CH<sub>2</sub>OR<sub>2</sub> or



in which R<sub>2</sub> is a lower alkyl group, X and Y being simultaneously not hydrogen; R<sub>1</sub> is a cyano group, a cyano(lower)alkyl group or a group of the formula: —CH<sub>2</sub>R<sub>5</sub>,



or —SO<sub>2</sub>R<sub>7</sub> in which R<sub>5</sub> is a lower alkylthio group, R<sub>6</sub> is a lower alkyl group, a lower alkoxy group or a lower alkylamino group and R<sub>7</sub> is a lower alkyl group, a halo(lower)alkyl group or a lower alkylamino group; A is an oxygen atom or a sulfur atom and B is a group of the formula: —W-R<sub>10</sub> in which W is an oxygen atom or a sulfur atom and R<sub>10</sub> is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a halo(lower)alkyl group or a lower alkoxy(lower)alkyl group.

Thus, the present invention provides a fungicidal aniline derivative of the formula (I). It also provides a fungicidal composition which comprises, as an active ingredient, a fungicidally effective amount of the compound (I) and an inert carrier or diluent. It also provides a combination composition comprising as active ingredients the compound (I) together with at least one of benzimidazole, thiophanate and/or cyclic imide fungicides, which is fungicidally effective against not only drug-sensitive fungi but also drug-resistant fungi, and hence particularly effective for the prevention of plant diseases. It further provides a method of controlling

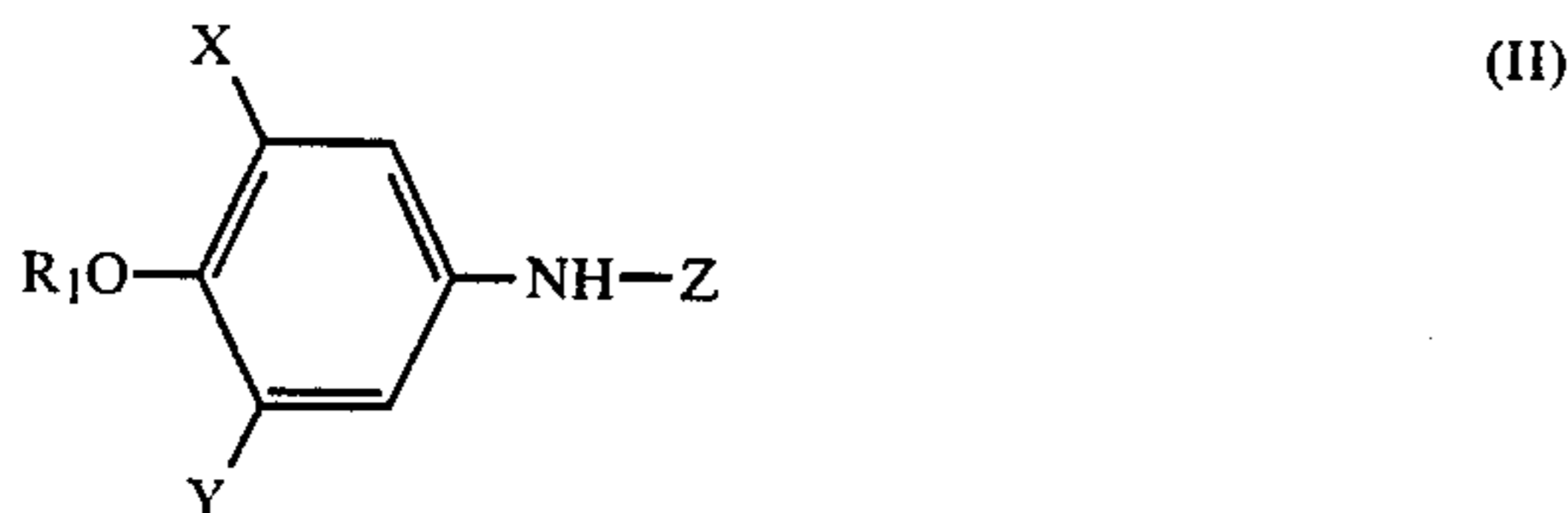
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plant pathogenic fungi including drug-resistant strains and drug-sensitive strains applying a fungicidally effective amount of the compound (I) to plant pathogenic fungi. It furthermore provides a process for producing the compound (I).

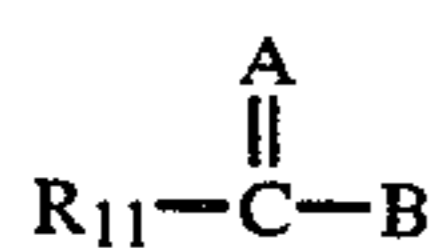
The compound of the formula (I) may be prepared by any one of the following procedures:

Procedure (a):

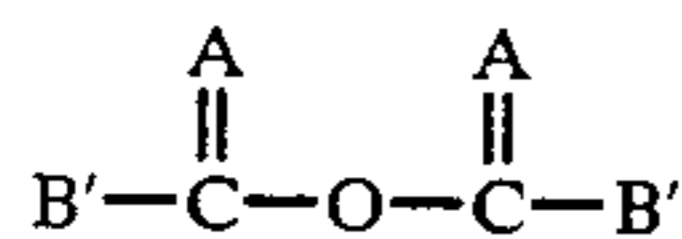
The compound (I) is prepared by reacting a compound of the formula:



wherein X, Y, R<sub>1</sub> and Z are each as defined above, with a halide of the formula:



wherein A and B are each as defined above and R<sub>11</sub> is a halogen atom, or with an anhydride of the formula:

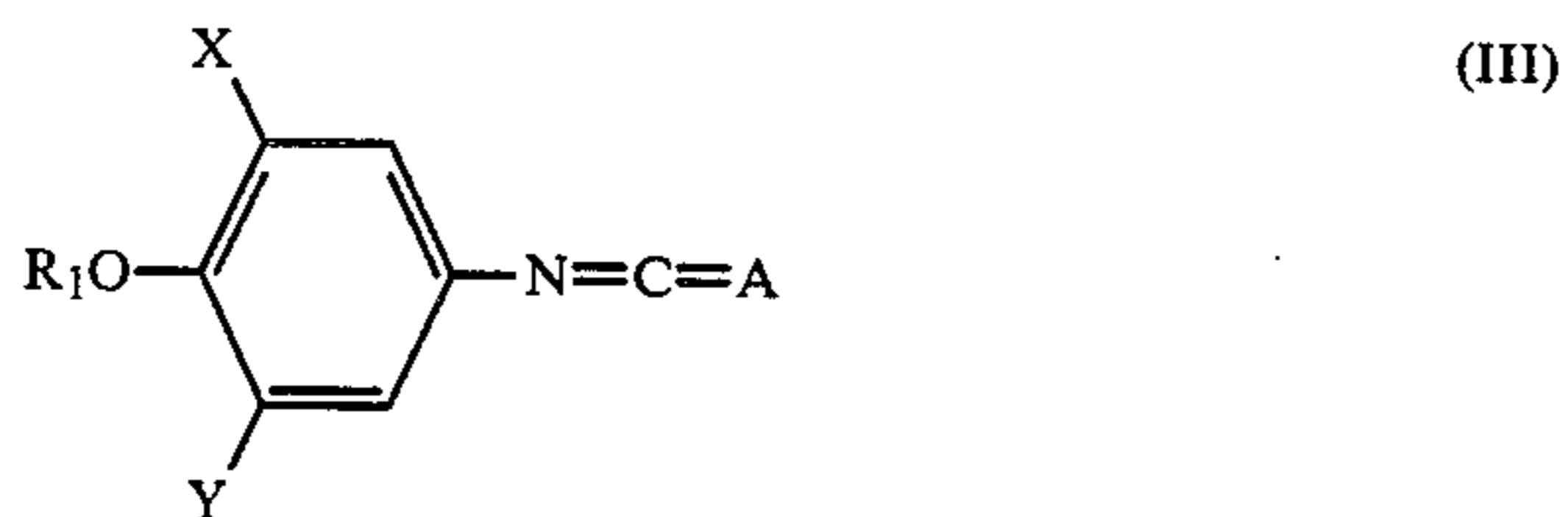


wherein A is as defined above and B' is a lower alkyl group, a lower alkenyl group, a lower cycloalkyl group or a phenyl group.

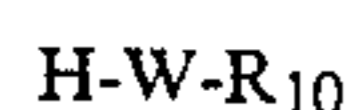
The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, tetrahydrofuran, chloroform, ethyl acetate, dimethylformamide). If desired, the reaction may be performed in the existence of a base (e.g. triethylamine, sodium hydroxide, N,N-diethylaniline) so as to obtain the compound (I) in a high yield. The reaction may be accomplished at a temperature of 0° to 150° C. instantaneously or within 12 hours.

Procedure (b):

The compound of the formula (I) wherein Z is a hydrogen atom and B is a group of the formula: -W-R<sub>10</sub> in which W and R<sub>10</sub> are each as defined above is also prepared by reacting a compound of the formula:



wherein X, Y, R<sub>1</sub> and A are each as defined above, with an alcohol or thioalcohol of the formula:



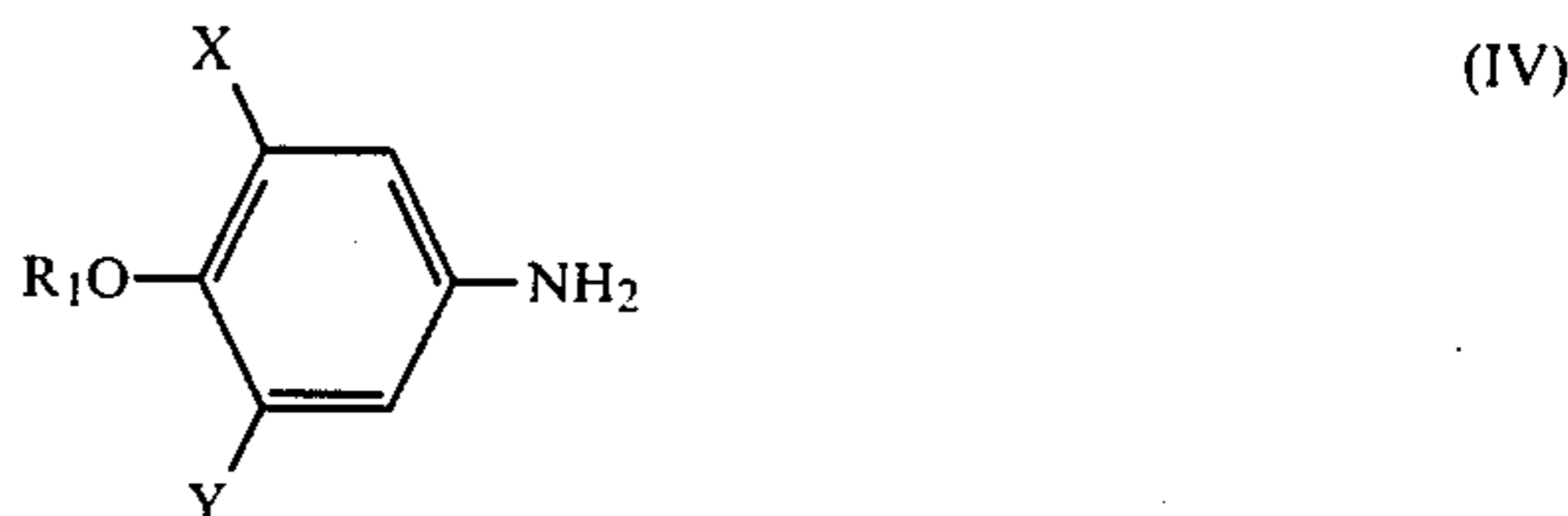
wherein W and R<sub>10</sub> are each as defined above.

The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, dimethylformamide, chloroform, carbon tetrachloride). If desired, the reaction may be performed in the existence of a catalyst (e.g. triethylamine, N,N-diethylaniline, 1,4-diazabicyclo[2.2.2]octane) so as to obtain the compound (I) in a

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high yield. The reaction may be accomplished at a temperature of 0° to 50° C. instantaneously or within 10 hours.

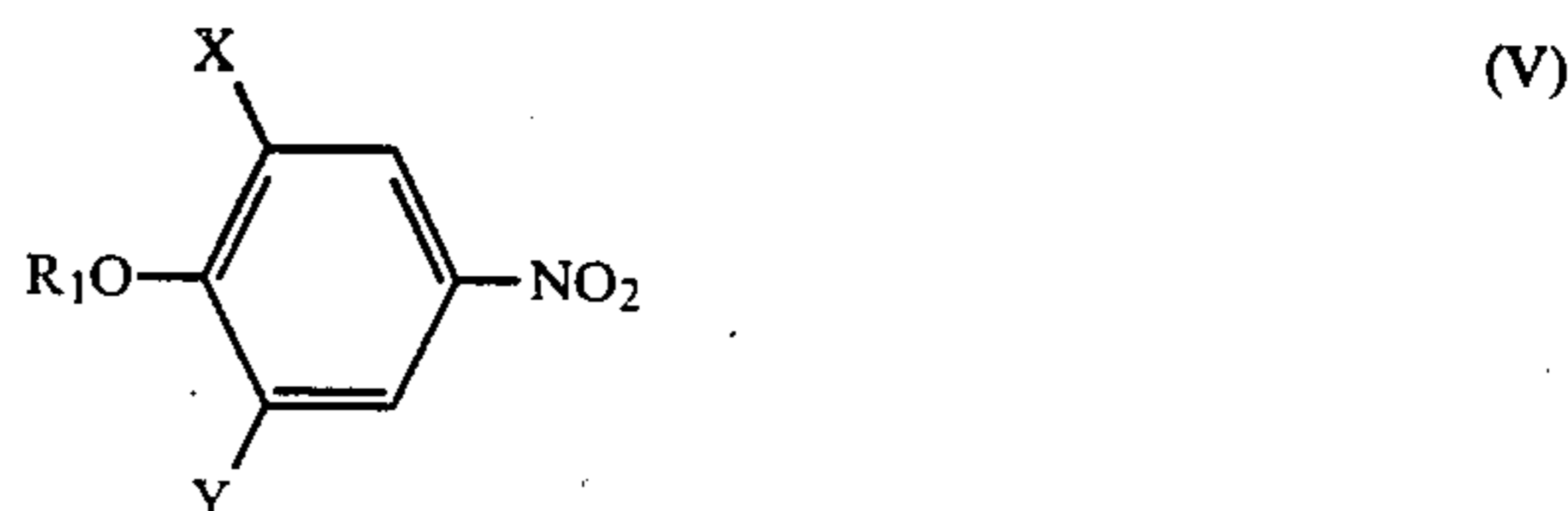
The starting compound (III) can be prepared by reacting a compound of the formula:



wherein X, Y and R<sub>1</sub> are each as defined above with phosgene or thiophosgene.

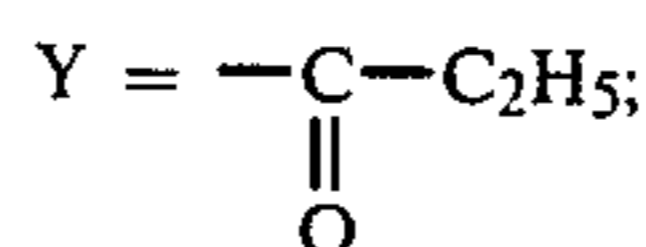
The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, xylene, ethyl acetate). The reaction may be accomplished at a temperature of 50° C. to the boiling point of the solvent instantaneously or within 10 hours.

The compound (IV) can be prepared by reduction of a nitrobenzene of the formula:



wherein X, Y and R<sub>1</sub> are each as defined above according to a conventional reduction procedure. A typical example of such reduction procedure is illustratively shown below.

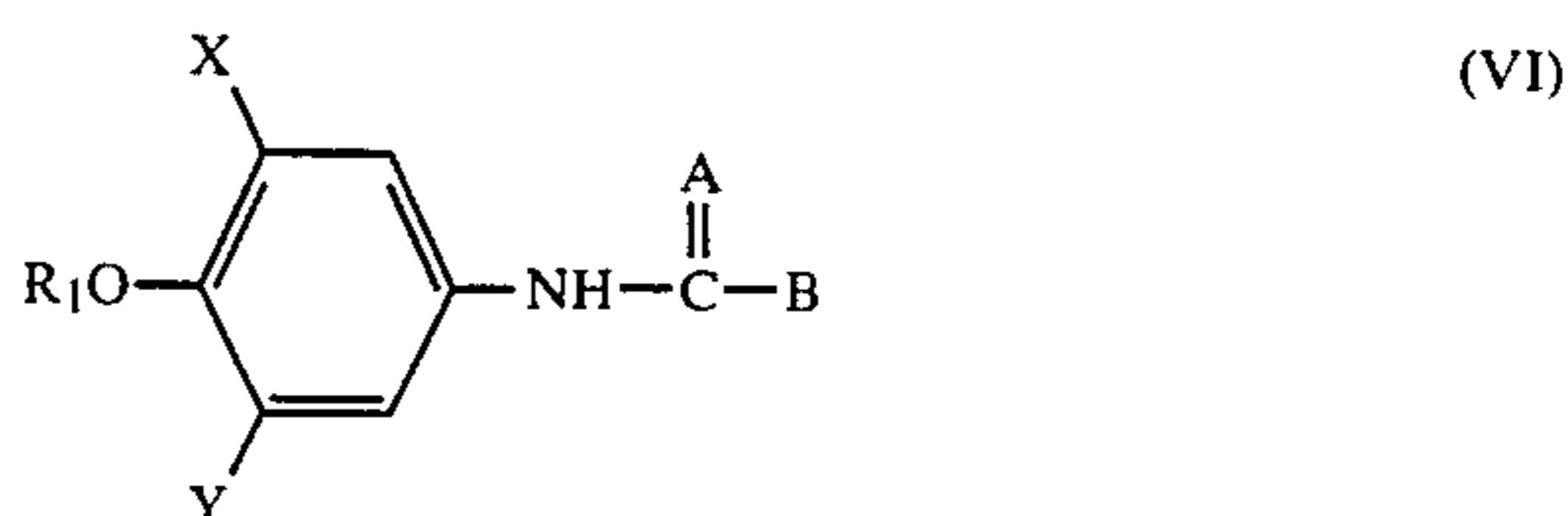
3-Propionyl-4-cyanomethoxy-5-methylnitrobenzene (X = CH<sub>3</sub>;



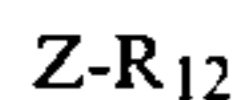
R<sub>1</sub> = -CH<sub>2</sub>C≡N) (4.96 g) in acetic acid (60 ml) was dropwise added to an aqueous solution (300 ml) containing acetic acid (15 ml) and iron (20 g). The resulting mixture was kept at 40° C. for 4 hours with vigorous stirring. The solid was removed by filtration, and the filtrate was extracted with dichloromethane. The extract was washed with an aqueous solution of potassium carbonate and water, dried over magnesium sulfate and concentrated under reduced pressure to give 3-propionyl-4-cyanomethoxy-5-methylaniline (3.88 g) in a yield of 88.8%. NMR δ (CDCl<sub>3</sub>): 1.18 (t, 3H), 2.30 (s, H), 2.85 (q, 2H), 4.61 (s, 2H), 6.68 (s, 2H).

Procedure (c):

The compound (I) is also prepared by reacting a compound of the formula:



wherein X, Y, R<sub>1</sub>, A and B are each as defined above, with a compound of the formula:

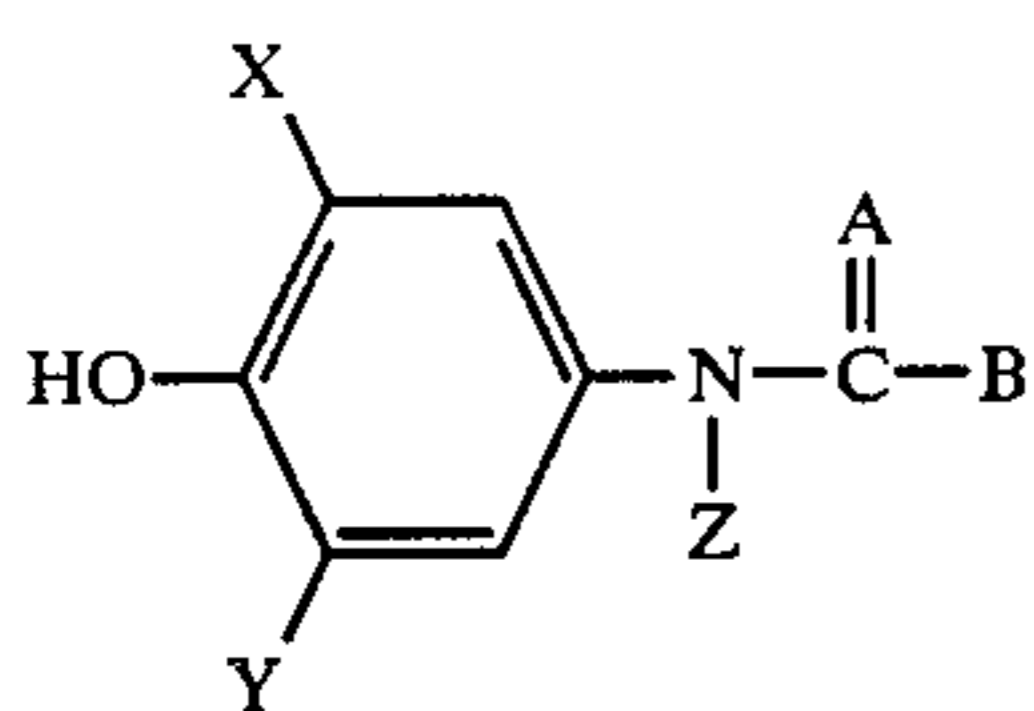


wherein Z is as defined above and R<sub>12</sub> is a leaving group (e.g. tosyloxy, mesyloxy, halogen).

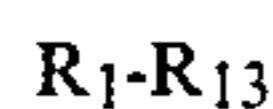
The reaction is usually carried out in the presence of an inert solvent (e.g. benzene, toluene, xylene, dioxane, chloroform). If desired, a base (e.g. triethylamine, sodium hydroxide, sodium hydride) may be present in the reaction system. The reaction may be accomplished at a temperature of 0° to 150° C. instantaneously or within 12 hours.

Procedure (d):

The compound (I) is also prepared by reacting a phenol of the formula:



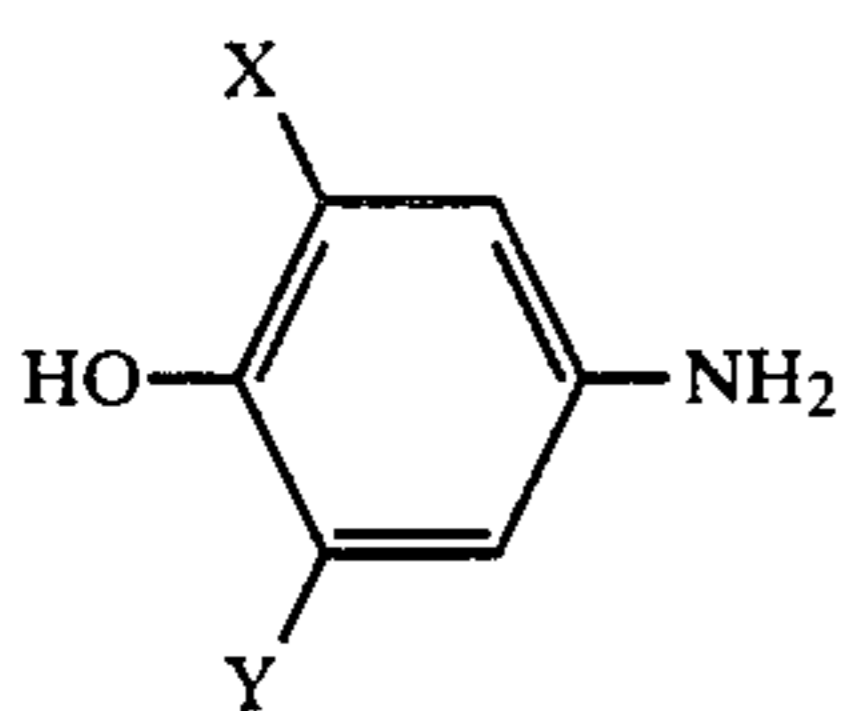
wherein X, Y, Z, A and B are each as defined above, with a compound of the formula:



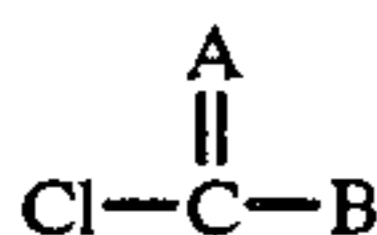
wherein R<sub>1</sub> is as defined above and R<sub>13</sub> is a leaving group (e.g. tosyloxy, mesyloxy, halogen).

The reaction is usually carried out in the absence or presence of an inert solvent (e.g. water, benzene, toluene, tetrahydrofuran, dimethylsulfoxide, dimethylformamide using a dehydrohalogenating agent (e.g. sodium hydroxide, potassium carbonate, sodium hydride) at a temperature of 10° to 100° C. for a period of 30 minutes to 12 hours.

The phenol of the formula (VII) wherein Z is a hydrogen atom can be prepared by reacting a 4-aminophenol of the formula:



wherein X and Y are each as defined above, with a chloride of the formula:



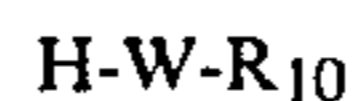
wherein A and B are each as defined above.

The reaction between the 4-aminophenol (VIII) and the chloride is usually carried out in an inert solvent (e.g. benzene, toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, chloroform, carbon tetrachloride, ethyl acetate, pyridine, dimethylformamide) in the presence of a dehydrohalogenating agent (e.g. pyridine, triethylamine, N,N-diethylaniline, sodium hydroxide, potassium hydroxide) at a temperature of 0 to 150° C. instantaneously or within 10 hours.

The phenol of the formula (VII) wherein Z is a hydrogen atom and B is a group of the formula: -W-R<sub>10</sub> in which W and R<sub>10</sub> are each as defined above, can be also prepared by reacting a 4-hydroxyphenyl isocyanate of the formula:



wherein X, Y and A are each as defined above, with an alcohol or thioalcohol of the formula:



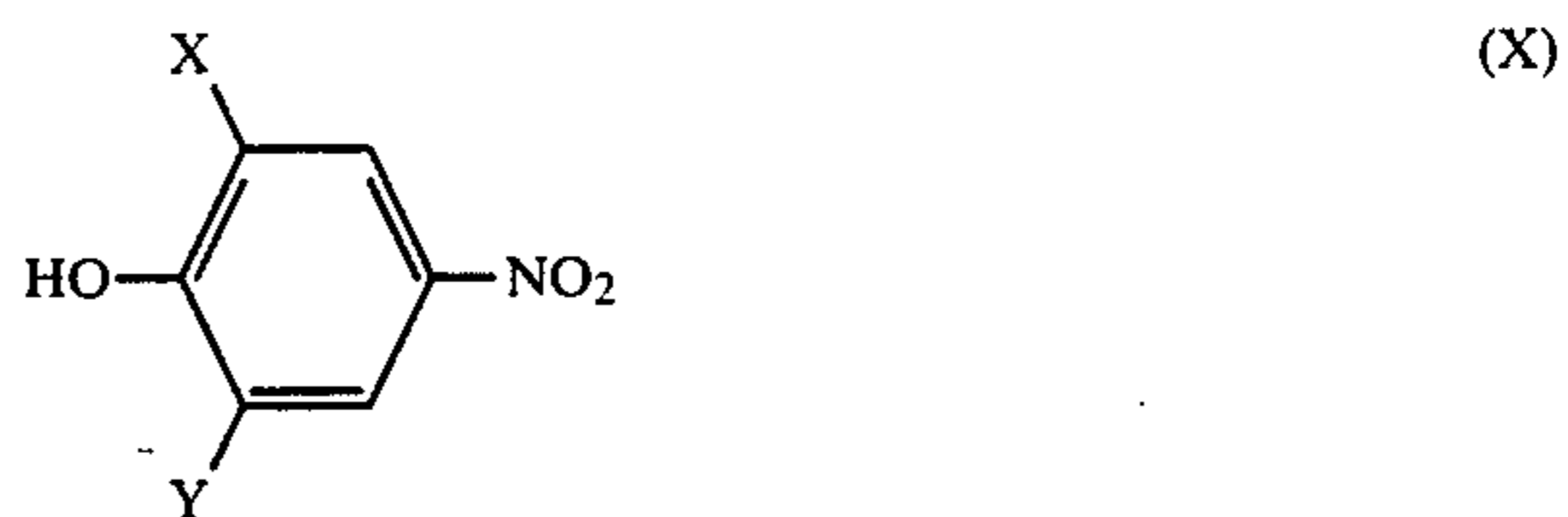
wherein W and R<sub>10</sub> are each as defined above.

The reaction between the 4-hydroxyphenyl isocyanate (IX) and the alcohol or thioalcohol can be carried out in the absence or presence of an inert solvent (e.g. toluene, xylene, diethyl ether, tetrahydrofuran, dioxane, dimethylformamide, chloroform, carbon tetrachloride). If desired, the reaction may be performed in the presence of a catalyst (e.g. triethylamine, N,N-diethylaniline 1,4-diazabicyclo[2.2.2]octane). The reaction is performed at a temperature of 0° to 50° C. instantaneously or within 10 hours.

Still, the 4-hydroxyphenyl isocyanate (IX) can be prepared by reacting the 4-aminophenol (VIII) with phosgene or thiophosgene.

The reaction between the 4-aminophenol (VIII) and phosgene or thiophosgene can be carried out in an inert solvent (e.g. benzene, toluene, ethyl acetate) at a temperature of 50° C. to the boiling point of the solvent within 30 minutes to 10 hours.

The aminophenol (VIII) can be prepared by reducing a 4-nitrophenol of the formula:

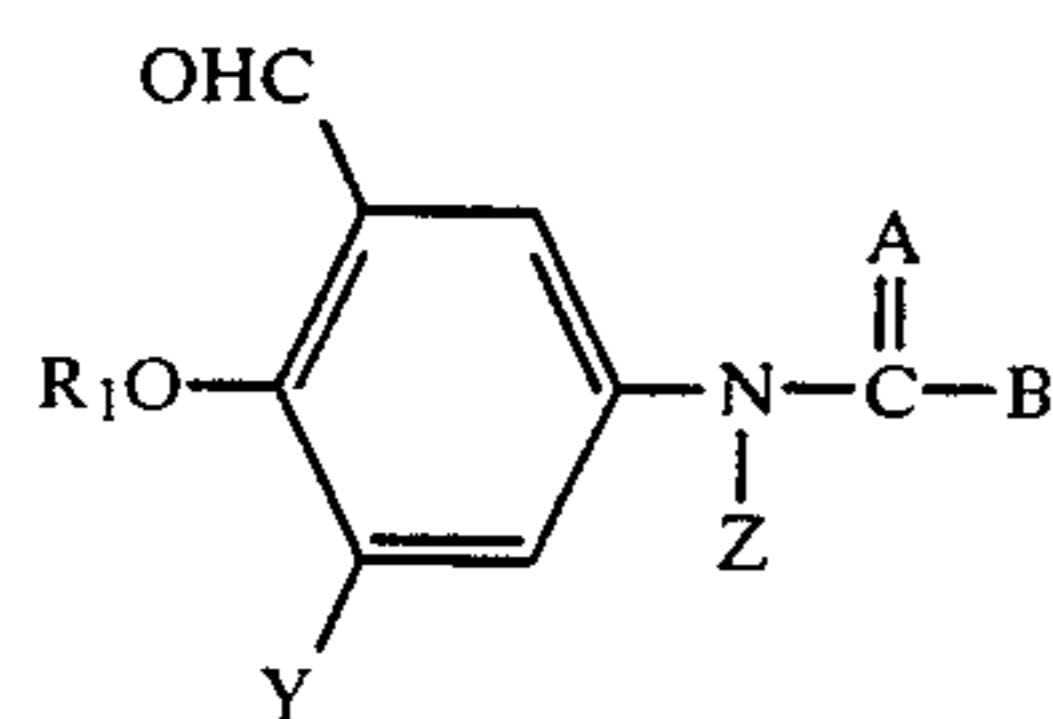


wherein X and Y are each as defined above according to a conventional reduction procedure. In case of catalytic hydrogenation, for example, the reaction may be carried out in an inert solvent (e.g. ethyl acetate, ethanol) in the presence of a catalyst (e.g. platinum oxide, palladium on carbon) at a temperature of 0° to 60° C. under hydrogen gas.

The 4-nitrophenol (X) can be prepared, for example, by the method described in the literature [J. Org. Chem., 27, 218 (1962)].

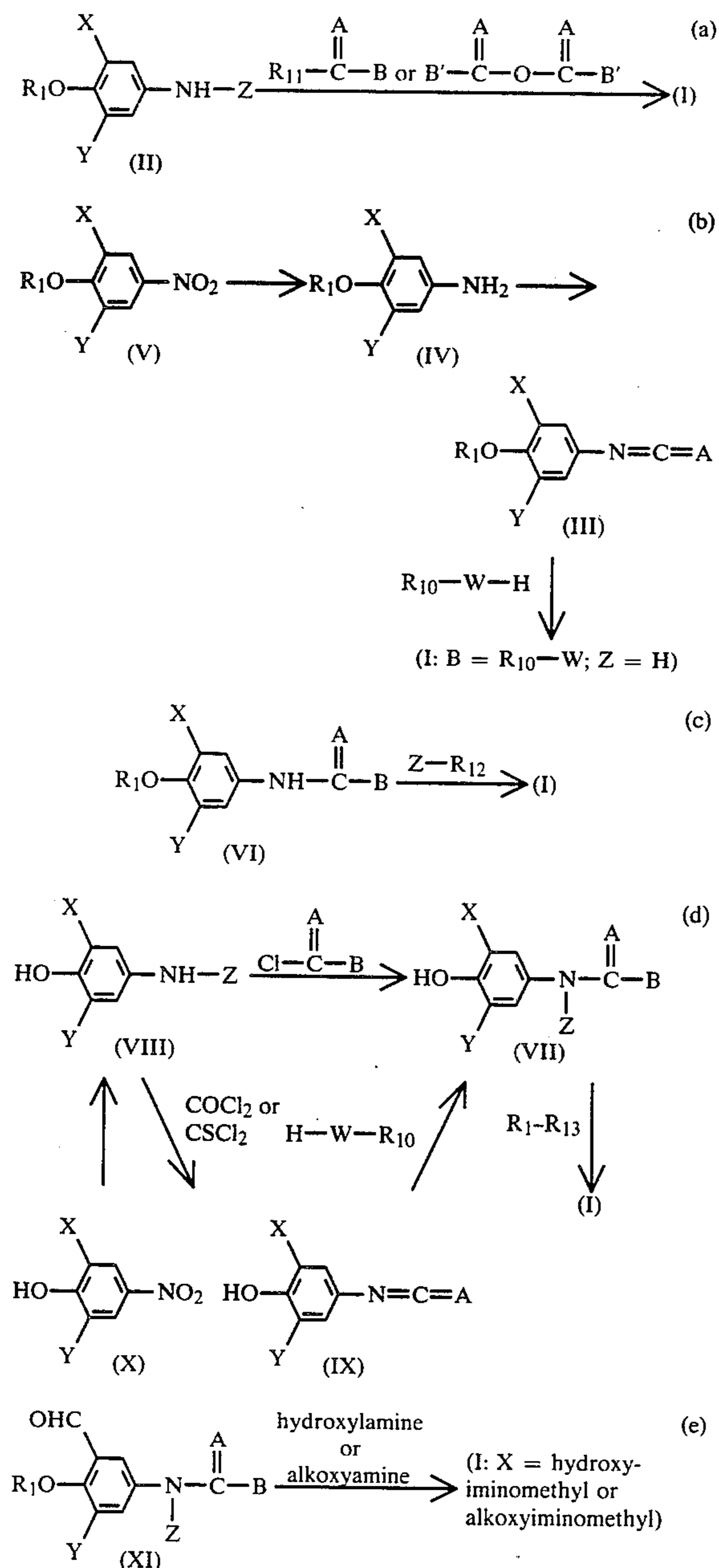
Procedure (e):

Further, the compound (I) wherein X is a hydroximinomethyl group or a lower alkoxyiminomethyl group can be prepared by reacting a benzaldehyde of the formula:



wherein Y, Z, A, B and R<sub>1</sub> are each as defined above, with an equimolar or excess amount of hydroxylamine or a lower alkoxyamine in an inert solvent (e.g. methanol, ethanol). The reaction may be brought to completion in about 0.5 to 12 hours.

The above-mentioned procedures are summarized in the following reaction scheme:



Some typical examples for preparation of the compound (I) are illustratively shown below.

## EXAMPLE 1

Preparation of isopropyl N-(3-chloro-4-methylcarbamoyloxy-5-methoxymethylphenyl)carbamate according to Procedure (a):

3-Chloro-4-methylcarbamoyloxy-5-methoxymethylphenylamine (1.0 g) and N,N-diethylaniline (0.90 g) were dissolved in toluene (15 ml). To the resultant solution was dropwise added isopropyl chloroformate (0.75 g) in 5 minutes under ice-cooling. The resultant mixture was allowed to stand at room temperature for 12 hours, poured into ice-water and extracted with ethyl acetate. The extract was washed with water, dried over magnesium sulfate and concentrated under reduced pressure.

The residue was purified by silica gel chromatography using a mixture of benzene and tetrahydrofuran as the eluent to give isopropyl N-(3-chloro-4-methylcarbamoyloxy-5-methoxymethylphenyl)carbamate (Compound No. 4) (1.22 g) in a yield of 90.5%. M.P., 113°-114° C.

Elementary analysis: Calcd. for C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>ClO<sub>5</sub>: C, 50.84%; H, 5.79%; N, 8.47%; Cl, 10.72%. Found: C, 50.81%; H, 5.88%; N, 8.35%; Cl, 10.92%.

## EXAMPLE 2

Preparation of isopropyl N-[3-chloro-4-(3-cyanopropoxy)-5-methoxymethylphenyl]carbamate according to Procedure (b):

3-Chloro-4-(3-cyanopropoxy)-5-methoxymethylphenylamine (2.55 g) in toluene (20 ml) was dropwise added to a toluene solution containing 10 g of phosgene at 10° to 20° C. The resulting mixture was gradually heated and, after being refluxed for 30 minutes, cooled to room temperature. The solvent was removed by distillation under reduced pressure to give 3-chloro-4-(3-cyanopropoxy)-5-methoxymethylphenyl isocyanate (2.80 g). The thus obtained crude substance was added to a toluene solution (50 ml) containing triethylamine (1.0 g) and isopropanol (1.0 g). The resultant mixture was allowed to stand at room temperature for 12 hours, poured into ice-water and extracted with ethyl acetate. The extract was washed with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using a mixture of toluene and ethyl acetate as the eluent to give isopropyl N-[3-chloro-4-(3-cyanopropoxy)-5-methoxymethylphenyl]carbamate (Compound No. 6) (2.70 g) in a yield of 79.2%. n<sub>D</sub><sup>20.0</sup> 1.5196.

NMR δ (CDCl<sub>3</sub>): 7.42 (d, 1H), 7.12 (d, 1H), 6.77 (broad, 1H), 4.92 (m, 1H), 4.45 (s, 2H), 3.95 (t, 2H), 3.37 (s, 3H), 2.65 (t, 2H), 2.18 (m, 2H), 1.25 (d, 6H).

## EXAMPLE 3

Preparation of isopropyl N-methyl-N-(3-chloro-4-cyanomethoxy-5-methoxymethylphenyl)carbamate according to Procedure (c):

Isopropyl N-(3-chloro-4-cyanomethoxy-5-methoxymethylphenyl)carbamate (3.13 g) and iodomethane (4.30 g) were dissolved in tetrahydrofuran (10 ml). The resultant solution was dropwise added to a tetrahydrofuran solution (20 ml) containing potassium hydroxide (1.68 g) and tetra-n-butylammonium bromide (1.0 g). After being allowed to stand at room temperature for 12 hours, the reaction mixture was poured into ice-water and extracted with toluene. The extract was washed with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified

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by silica gel chromatography using a mixture of toluene and ethyl acetate as the eluent to give isopropyl N-methyl-N-(3-chloro-4-cyanomethoxy-5-methoxymethylphenyl)carbamate (Compound No. 41) (3.06 g) in a yield of 93.5%.  $n_D^{22.0}$  1.5123.

## EXAMPLE 4

Preparation of isopropyl N-(3-chloro-4-cyanomethoxy-5-methoxymethylphenyl)carbamate according to Procedure (d):

3-Chloro-4-hydroxy-5-methoxymethylaniline (52.8 g) and N,N-diethylaniline (42.0 g) were dissolved in ethyl acetate (300 ml). To the resultant solution was dropwise added isopropyl chloroformate (34.6 g) in 15 minutes under ice-cooling. After being allowed to stand at room temperature for 12 hours, the reaction mixture was poured into ice-water. The organic layer was washed with dilute hydrochloric acid and water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using toluene and ethyl acetate as the eluent to give isopropyl N-(3-chloro-4-hydroxy-5-methoxymethylphenyl)carbamate (65.6 g). Sodium hydride (9.60 g, 60% dispersion in mineral oil) was added to dimethylformamide (240 ml). To the resultant mixture was added isopropyl N-(3-chloro-4-hydroxy-5-methoxymethylphenyl)carbamate (65.6 g) under 5° C. The resulting solution was stirred at a temperature of 20° C. for 30 minutes, and chloroacetonitrile (19.0 g) was added thereto in 5 minutes. The mixture was heated at 90° C. for 10 minutes, poured into ice-water and extracted with ethyl acetate. The extract was washed with aqueous potassium carbonate solution and water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using toluene and ethyl acetate as the eluent to give isopropyl N-(3-chloro-4-cyanomethoxy-5-methoxymethylphenyl)carbamate (Compound No. 5) (67.5 g) in a yield of 76.8%. M.P., 58.5°-60.5° C.

Elementary analysis: Calcd. for  $C_{14}H_{17}N_2O_4Cl$ : C, 53.77%; H, 5.48%; N, 8.96%; Cl, 11.34%. Found: C, 53.77%; H, 5.57%; N, 8.88%; Cl, 11.60%.

## EXAMPLE 5

Preparation of isopropyl N-(3-methyl-4-methylthiomethoxy-5-n-propylphenyl)carbamate according to Procedure (d):

A mixture of 3-methyl-4-hydroxy-5-n-propylaniline (1.65 g) and ethyl acetate (20 ml) was added to an ethyl acetate solution containing 10 g of phosgene at 0° to 5° C. The resulting mixture was gradually heated and, after the solution became clear, cooled to room temperature. The solvent was removed by distillation under

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reduced pressure to give 3-methyl-4-hydroxy-5-n-propylphenyl isocyanate. The thus obtained crude substance was added to a toluene solution (50 ml) containing triethylamine (1.0 g) and isopropanol (1.0 g). The resultant mixture was allowed to stand at room temperature for 12 hours, poured into ice-water and extracted with ethyl acetate. The extract was washed with dilute hydrochloric acid and water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using a mixture of toluene and ethyl acetate as the eluent to give isopropyl N-(3-methyl-4-hydroxy-5-n-propylphenyl)carbamate (1.70 g). Sodium hydride (0.28 g, 60% dispersion in mineral oil) was added to dimethylformamide (50 ml). To the resulting mixture was added isopropyl N-(3-methyl-4-hydroxy-5-n-propylphenyl)carbamate (1.70 g) under 5° C. The resulting solution was stirred at a temperature of 20° C. for 30 minutes, and (chloromethyl)methylsulfide (0.67 g) was added thereto in 5 minutes. The mixture was heated at 90° C. for 10 minutes, poured into ice-water and extracted with ethyl acetate. The extract was washed with aqueous potassium carbonate solution and water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography using a mixture of toluene and ethyl acetate as the eluent to give isopropyl N-(3-methyl-4-methylthiomethoxy-5-n-propylphenyl)carbamate (Compound No. 14) (1.90 g) in a yield of 61.0%.  $n_D^{21.4}$

NMR  $\delta$  ( $CDCl_3$ ): 7.01 (s, 2H), 6.45 (broad, 1H), 4.99 (m, 1H), 4.86 (s, 2H), 2.65 (t, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 1.29 (d, 6H), 0.80-1.50 (m, 5H).

## EXAMPLE 6

Preparation of isopropyl N-(3-methoxy-4-cyanomethoxy-5-methoxyiminomethylphenyl)carbamate according to Procedure (e):

Isopropyl N-(3-methoxy-4-cyanomethoxy-5-formylphenyl)carbamate (0.59 g) was dissolved in ethanol (20 ml). To the solution was added an aqueous solution (10 ml) containing sodium hydroxide (0.32 g) and methoxyamine hydrochloride (0.66 g). After being allowed to stand for 12 hours, the reaction mixture was concentrated in vacuo, and the residue was dissolved in ethyl acetate. The resultant solution was washed with water, dried over magnesium sulfate and concentrated under reduced pressure to give isopropyl N-(3-methoxy-4-cyanomethoxy-5-methoxyiminomethylphenyl)carbamate (Compound No. 78) (0.62 g) in a yield of 94.5%.

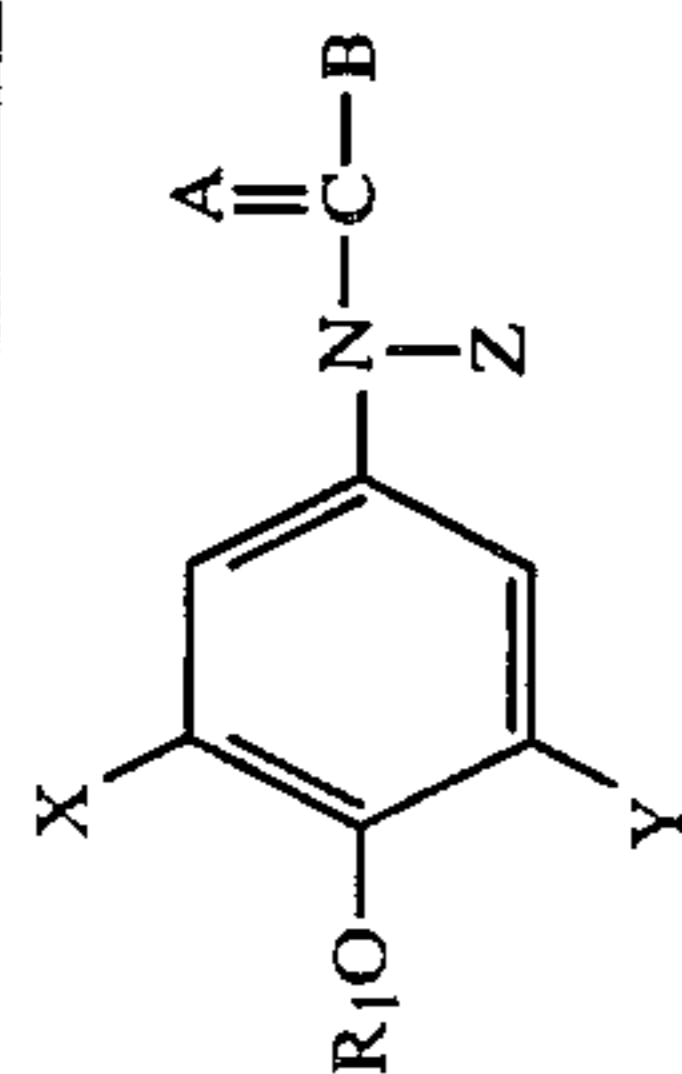
According to any one of Procedures (a), (b), (c), (d) and (e), the aniline derivatives of the formula (I) as shown in Table 1 can be prepared:

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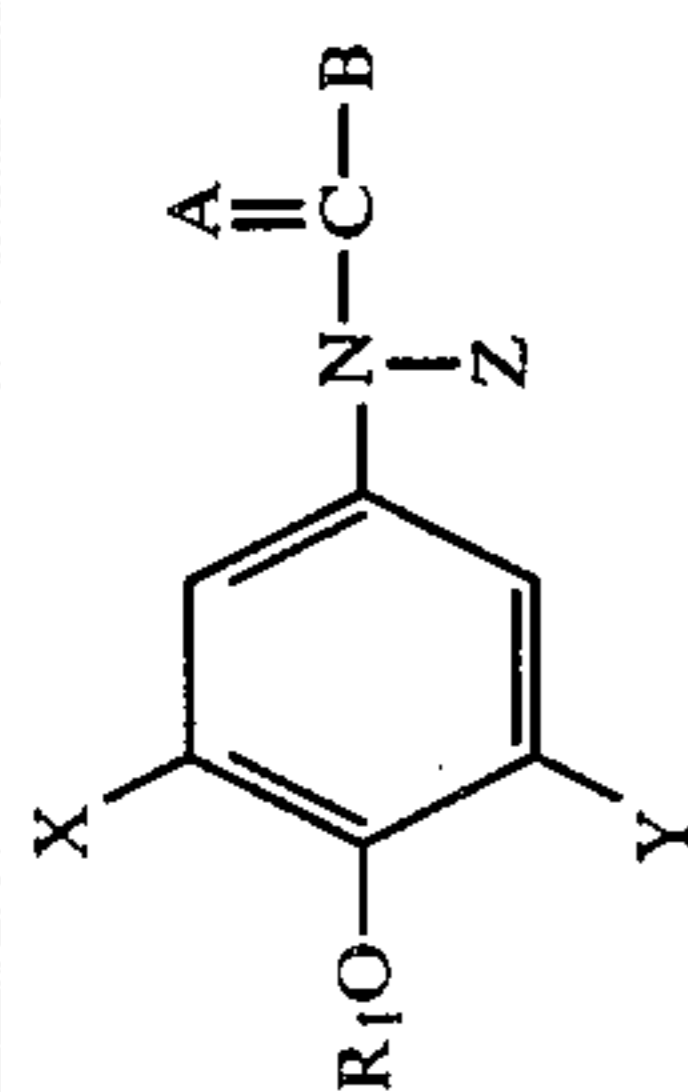
TABLE I



Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
1	-H	-OC <sub>2</sub> H <sub>5</sub>	-C(=O)O(i)Pr	-H	O	-O(i)Pr	M.P. 93-94° C.
2	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-C(=O)CH <sub>3</sub>	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>26.1</sup> 1.5142
3	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-C(=O)OCH <sub>3</sub>	-H	O	-O(i)Pr	M.P. 90-92° C.
4	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-C(=O)NHCH <sub>3</sub>	-H	O	-O(i)Pr	M.P. 113-114° C.
5	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	M.P. 58.5-60.5° C.
6	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-(CH <sub>2</sub> ) <sub>3</sub> C≡N	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>20.0</sup> 1.5196
7	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> SCH <sub>3</sub>	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>20.0</sup> 1.5471
8	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-SO <sub>2</sub> CH <sub>3</sub>	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>22.0</sup> 1.5266
9	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-SO <sub>2</sub> CF <sub>3</sub>	-H	O	-O(i)Pr	M.P. 96-98° C.
10	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-SO <sub>2</sub> NH-(n)Pr	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>22.0</sup> 1.5250
11	-CH <sub>3</sub>	-CH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	M.P. 114-116° C.
12	-CH <sub>3</sub>	-C(=O)OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	M.P. 76-78° C.
13	-Cl	-OC <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	M.P. 89-91° C.
14	-CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> SCH <sub>3</sub>	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>21.4</sup> 1.5299
15	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH-CH=CH <sub>2</sub>   CH <sub>3</sub>	<i>n</i> <sub>D</sub> <sup>22.0</sup> 1.5383
16	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH-C≡CH   C <sub>2</sub> H <sub>5</sub>	<i>n</i> <sub>D</sub> <sup>19.7</sup> 1.5350

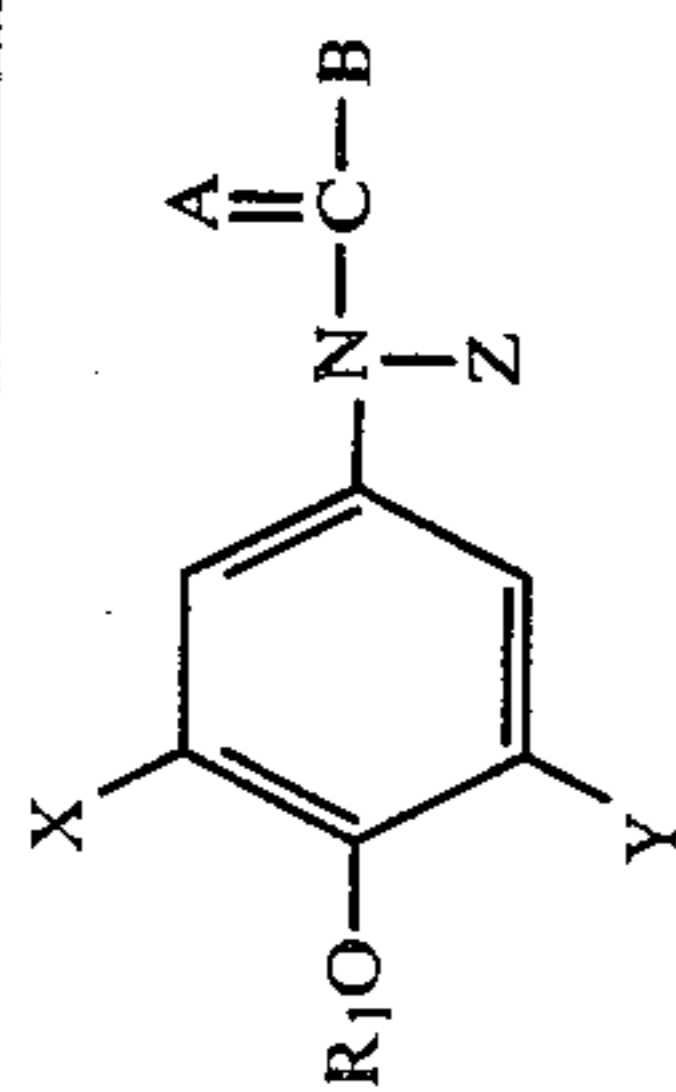


TABLE 1-continued



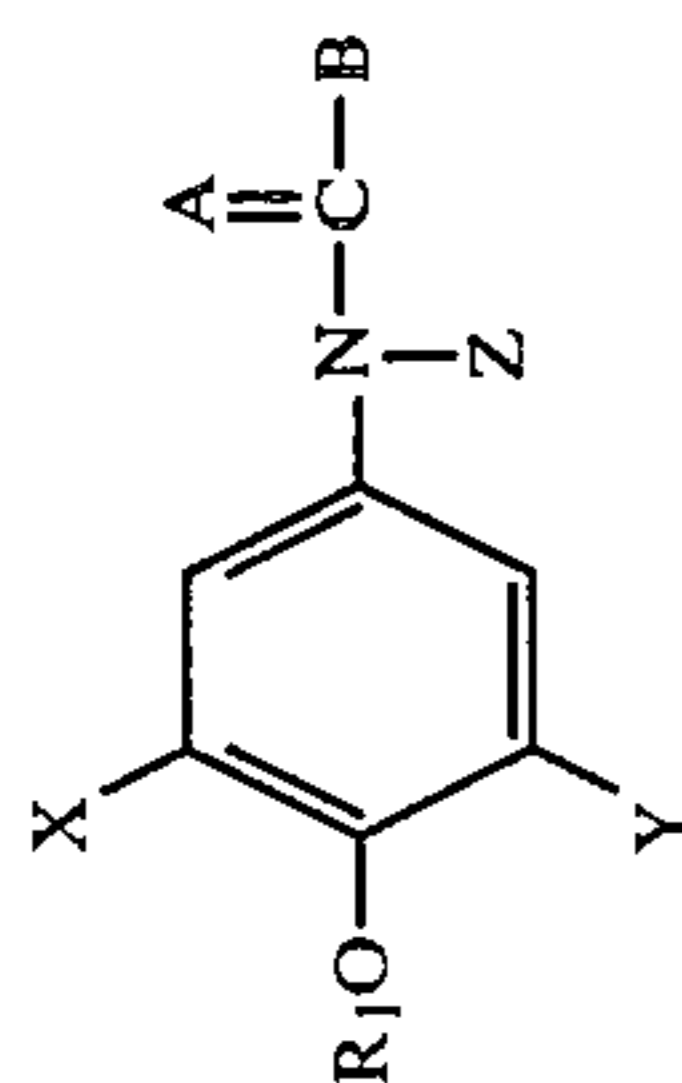
Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
17	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH-CH <sub>3</sub>   CH <sub>2</sub> OCH <sub>3</sub>	<i>n</i> <sub>D</sub> <sup>22.0</sup> 1.5191
18	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> CH <sub>2</sub> F	<i>n</i> <sub>D</sub> <sup>22.0</sup> 1.5280
19	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-SC <sub>2</sub> H <sub>5</sub>	<i>n</i> <sub>D</sub> <sup>22.0</sup> 1.5752
20	-CH <sub>3</sub>	-CH <sub>2</sub> CH=CH <sub>2</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>22.3</sup> 1.5275
21	-CH <sub>3</sub>	-C(=O)-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
22	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	S	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>20.5</sup> 1.5733
23	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	S	-S(i)Pr	<i>n</i> <sub>D</sub> <sup>20.5</sup> 1.5838
24	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-C≡N	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>23.0</sup> 1.5268
25	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>20.8</sup> 1.5530
26	-Br	-Br	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	M.P. 143-144° C.
27	-Br	-C≡CH	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 1.21(d, 6H), 3.30(s, 1H), 4.70(s, 2H), 5.00(m, 1H), 7.25-7.80(3H)
28	-Br	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
29	-Cl	-NH-C(=O)-CH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
30	-Cl	-NH-C(=O)-OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
31	-Cl	-NH-C(=O)-NHCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
32	-Cl	-N=CHCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
33	-OC <sub>2</sub> H <sub>5</sub>	-C≡CH	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
34	-OC <sub>2</sub> H <sub>5</sub>	-C≡N	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
35	-CH <sub>3</sub>	-C(=O)-OCH <sub>2</sub>   CH=CH <sub>2</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	<i>n</i> <sub>D</sub> <sup>22.5</sup> 1.5290

TABLE I-continued



Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
36	-CH <sub>3</sub>	-C(=O)OCH <sub>2</sub>   O C≡CH	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	M.P. 85-87° C.
37	-CH(OCH <sub>3</sub> ) <sub>2</sub>	-OC <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 1.25(t, 6H), 1.30(d, 6H), 3.65(d, 4H), 3.91(s, 3H), 4.80(s, 2H), 5.05(m, 1H), 5.78(s, 1H), 6.88(d, 1H), 7.58(d, 1H)
38	-CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	-OC <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
39	-CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	-OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
40	-CH <sub>3</sub>	-CH <sub>2</sub> -C(=O)-CH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
41	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-CH <sub>3</sub>	O	-O(i)Pr	n <sub>D</sub> <sup>22.0</sup> 1.5123 n <sub>D</sub> <sup>20.8</sup> 1.5193 n <sub>D</sub> <sup>20.0</sup> 1.5170 NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 1.20(d, 6H), 2.60(s, 3H), 3.40(s, 3H), 4.54(s, 2H), 4.84(s, 2H), 5.00(m, 1H), 7.14(s, 2H)
42	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-CH <sub>2</sub> CH=CH <sub>2</sub>	O	-O(i)Pr	
43	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-CH <sub>2</sub> C≡CH	O	-O(i)Pr	
44	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-C(=O)-CH <sub>3</sub>	O	-O(i)Pr	
45	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N		O	-O(i)Pr	NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 0.70-1.30 (m, 4H), 1.30(d, 6H), 2.80- 3.10(m, 1H), 3.45(s, 3H), 4.55(s, 2H), 4.81(s, 2H), 4.98(m, 1H), 7.12(s, 2H) n <sub>D</sub> <sup>20.8</sup> 1.5513
46	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-C(=O)-C <sub>6</sub> H <sub>5</sub>	O	-O(i)Pr	
47	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-C(=O)-CH <sub>2</sub> Cl	O	-O(i)Pr	
48	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-C(=O)-CH <sub>2</sub> OCH <sub>3</sub>	O	-O(i)Pr	

TABLE I-continued


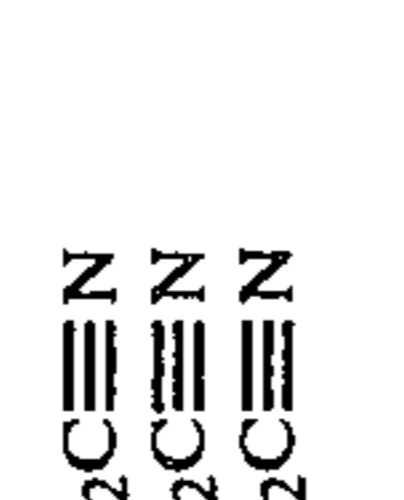


Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
49	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-CH-COOCH <sub>3</sub>   CH <sub>3</sub>	O	-O(i)Pr	
50	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-CH <sub>2</sub> COOCH <sub>3</sub>	O	-O(i)Pr	$n_D^{23.2}$ 1.5075
51	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-SCH <sub>3</sub>	O	-O(i)Pr	$n_D^{22.5}$ 1.5583
52	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-SC <sub>6</sub> H <sub>5</sub>	O	-O(i)Pr	
53	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-S-C-O    O C <sub>2</sub> H <sub>5</sub>	O	-O(i)Pr	$n_D^{23.2}$ 1.5221
54	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-S-C-OCH <sub>3</sub>    O	O	-O(i)Pr	
55	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-OH	O	-O(i)Pr	
56	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-CH   CH <sub>3</sub>   C <sub>2</sub> H <sub>5</sub>	$n_D^{24.0}$ 1.5341
57	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-OCH <sub>3</sub>	O	-O(i)Pr	
58	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-O-C-CH <sub>3</sub>    O	O	-O(i)Pr	
59	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-O-C-OCH <sub>3</sub>    O	O	-O(i)Pr	
60	-CH <sub>3</sub>	-C-SCH <sub>3</sub>    O	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
61	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O		$n_D^{24.0}$ 1.5434

TABLE 1-continued

Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
62	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-CH=CHCH <sub>3</sub>	$n_D^{24.0}$ 1.5526
63	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-C <sub>6</sub> H <sub>5</sub>	M.P. 101-102° C.
64	-CH <sub>3</sub>	-CH <sub>2</sub> CNBrCH <sub>2</sub> Br	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	NMR $\delta_{7MS}^{CDCl_3}$ : 1.30(d, 6H), 2.34(s, 3H), 4.63(s, 2H), 6.84(broad, 1H), 7.20(s, 2H)
65	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> CH=CH-   CH <sub>2</sub> Cl	$n_D^{22.6}$ 1.5400
66	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> -   C≡CCH <sub>2</sub> Cl	$n_D^{23.8}$ 1.5338
67	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O		
68	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O		
69	-CH <sub>3</sub>	-O-CH <sub>2</sub> -   CH=CH <sub>2</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
70	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> CH <sub>2</sub> C≡N	M.P. 95-97° C.
71	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O		$n_D^{28.9}$ 1.5473

TABLE 1-continued

Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
72	-CH <sub>3</sub>	-O-CH <sub>3</sub>   C≡CH	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
73	-CH <sub>3</sub>	-CH=NOCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 1.25(d, 6H), 3.74(s, 3H), 3.80-4.00 (m, 4H), 4.68(s, 2H), 5.92(s, 1H), 6.78(d, 1H), 7.30(d, 1H)
74	-CH <sub>3</sub>	-OC <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
75	-OCH <sub>3</sub>		-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
76	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	n <sub>D</sub> <sup>17.5</sup> 1.5218 NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 1.25(d, 6H), 3.82(s, 3H), 4.35(s, 2H), 8.30(s, 1H)
77	-OCH <sub>3</sub>	-CH=NOH	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
78	-OCH <sub>3</sub>	-CH=NOCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	NMR δ <sub>TMS</sub> <sup>CDCl<sub>3</sub></sup> : 1.30(d, 6H), 3.88(s, 1H), 4.76(s, 2H), 8.42(s, 1H)
79	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O		n <sub>D</sub> <sup>21.8</sup> 1.5190
80	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> CH <sub>2</sub>   OCH <sub>2</sub> CH=CH <sub>2</sub>	n <sub>D</sub> <sup>21.8</sup> 1.5316
81	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> CH <sub>2</sub>   OCH <sub>2</sub> CH <sub>2</sub> Cl	n <sub>D</sub> <sup>21.9</sup> 1.5310
82	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCHCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub>   CH <sub>3</sub>	n <sub>D</sub> <sup>22.4</sup> 1.5483
83	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	-OCH <sub>2</sub> CH <sub>2</sub>   OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	n <sub>D</sub> <sup>22.8</sup> 1.5426

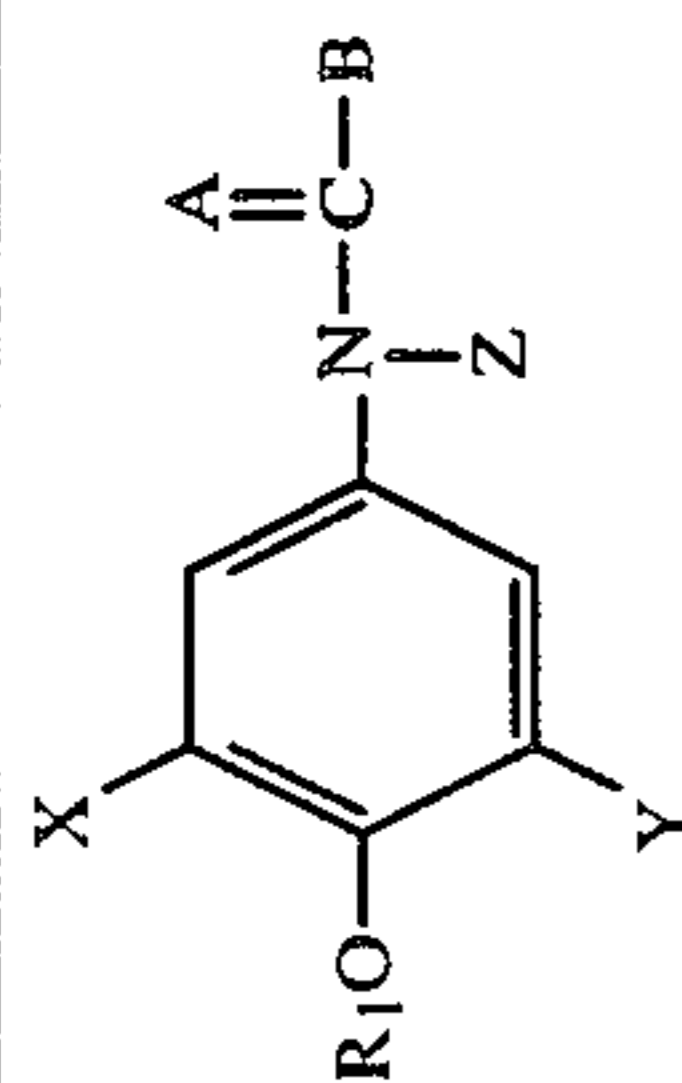
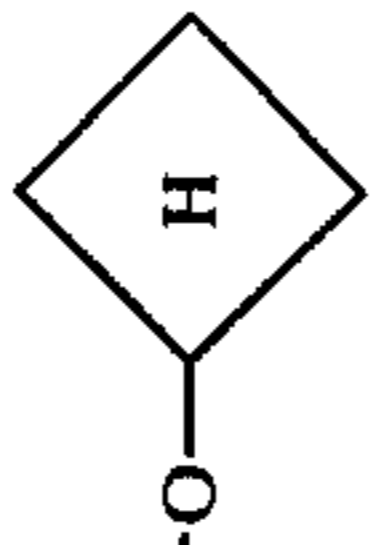
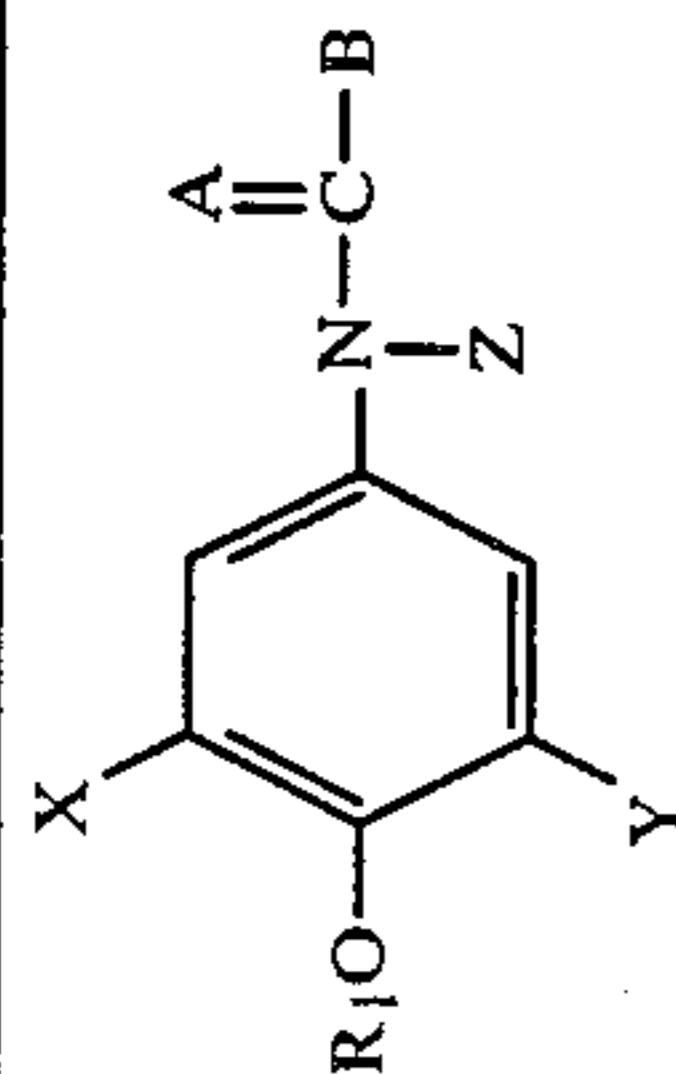


TABLE 1-continued

Compound No.	X	Y	R <sub>1</sub>	Z	A	B	Physical Constant
84	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	$\begin{array}{c} \text{CH}_2\text{OCH}_3 \\   \\ -\text{OCH} \\   \\ \text{CH}_2\text{Cl} \end{array}$	n <sub>D</sub> <sup>21.8</sup> 1.5221
85	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O		n <sub>D</sub> <sup>22.7</sup> 1.5230
86	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	$\begin{array}{c} -\text{OCH}-\text{C}\equiv\text{CH} \\   \\ \text{CH}_3 \end{array}$	n <sub>D</sub> <sup>23.8</sup> 1.5307
87	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> CH=CH-   CH <sub>2</sub> Cl	-H	O	-O(i)Pr	n <sub>D</sub> <sup>31.0</sup> 1.5306
88	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡C-   CH <sub>2</sub> Cl	-H	O	-O(i)Pr	n <sub>D</sub> <sup>31.0</sup> 1.5365
89	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> -C(=O)-OCH <sub>3</sub>	-H	O	-O(i)Pr	n <sub>D</sub> <sup>26.0</sup> 1.5181
90	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> -C(=O)-CH <sub>3</sub>	-H	O	-O(i)Pr	n <sub>D</sub> <sup>26.0</sup> 1.5259
91	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> OH	-H	O	-O(i)Pr	n <sub>D</sub> <sup>23.0</sup> 1.5200
92	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> CH=CHCH <sub>2</sub> OCH <sub>3</sub>	-H	O	-O(i)Pr	n <sub>D</sub> <sup>24.4</sup> 1.5193
93	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡CCH <sub>2</sub> OCH <sub>3</sub>	-H	O	-O(i)Pr	n <sub>D</sub> <sup>24.4</sup> 1.5297
94	-Cl	-CH <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> C≡N	-H	O	$\begin{array}{c} \text{CH}_2\text{Cl} \\   \\ -\text{OCH} \\   \\ \text{CH}_2\text{Cl} \end{array}$	
95	-OC <sub>2</sub> H <sub>5</sub>	-CHBrCH <sub>2</sub> Br	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	
96	-CH <sub>3</sub>	-CH=NOH	-CH <sub>2</sub> C≡N	-H	O	-O(i)Pr	



In the practical usage of the compounds of the formula (I) as fungicides, they may be applied as such or in a formulation form such as dusts, wettable powders, oil sprays, emulsifiable concentrates, tablets, granules, fine granules, aerosols or flowables. Such formulation form can be formulated in a conventional manner by mixing at least one of the compounds of the formula (I) with an appropriate solid or liquid carrier(s) or diluent(s) and, if necessary, an appropriate adjuvant(s) (e.g. surfactants, adherents, dispersants, stabilizers) for improving the dispersibility and other properties of the active ingredient.

Examples of the solid carriers or diluents are botanical materials (e.g. flour, tobacco stalk powder, soybean powder, walnut-shell powder, vegetable powder, saw dust, bran, bark powder, cellulose powder, vegetable extract residue), fibrous materials (e.g. paper, corrugated cardboard, old rags), synthetic plastic powders, clays (e.g. kaolin, bentonite, fuller's earth), talcs, other inorganic materials (e.g. pyrophyllite, sericite, pumice, sulfur powder, active carbon) and chemical fertilizers (e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, urea, ammonium chloride).

Examples of the liquid carriers or diluents are water, alcohols (e.g. methanol, ethanol), ketones (e.g. acetone, methylethylketone), ethers (e.g. diethyl ether, dioxane, cellosolve, tetrahydrofuran), aromatic hydrocarbons (e.g. benzene, toluene, xylene, methyl naphthalene), aliphatic hydrocarbons (e.g. gasoline, kerosene, lamp oil), esters, nitriles, acid amides (e.g. dimethylformamide, dimethylacetamide), halogenated hydrocarbons (e.g. dichloroethane, carbon tetrachloride), etc.

Examples of the surfactants are alkyl sulfuric esters, alkyl sulfonates, alkylaryl sulfonates, polyethylene glycol ethers, polyhydric alcohol esters, etc. Examples of the adherents and dispersants may include casein, gelatin, starch powder, carboxymethyl cellulose, gum arabic, alginic acid, lignin, bentonite, molasses, polyvinyl alcohol, pine oil and agar. As the stabilizers, there may be used PAP (isopropyl acid phosphate mixture), tricresyl phosphate (TCP), tolu oil, epoxydized oil, various surfactants, various fatty acids and their esters, etc.

The foregoing formulations generally contain at least one of the compounds of the formula (I) in a concentration of about 1 to 95% by weight, preferably of 2.0 to 80% by weight. By using the formulations, the compounds of the formula (I) are generally applied in such amounts as 2 to 100 g per 10 are.

When only the drug-resistant strains of phytopathogenic fungi are present, the compounds of the formula (I) may be used alone. However, when the drug-sensitive strains are present together with the drug-resistant strains, their alternate use with benzimidazole, thiophanate and/or cyclic imide fungicides or their combined use with benzimidazole, thiophanate and/or cyclic imide fungicides is favorable. In such alternate or combined use, each active ingredient may be employed as such or in conventional agricultural formulation forms. In case of the combined use, the weight proportion of the compound of the formula (I) and the benzimidazole, thiophanate and/or cyclic imide fungicide may be from about 1:0.1 to 1:10.0.

Typical examples of the benzimidazole, thiophanate and cyclic imide fungicides are shown in Table 2.

TABLE 2

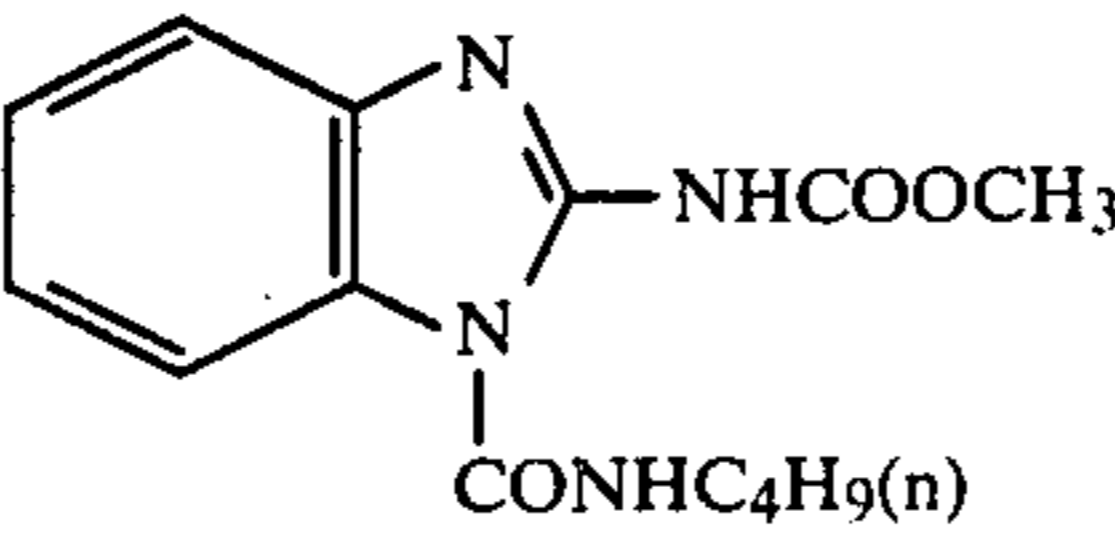
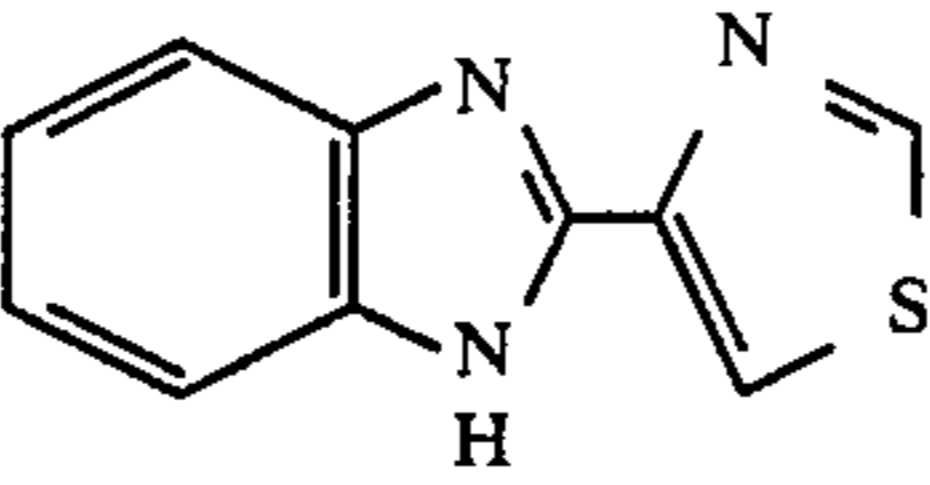
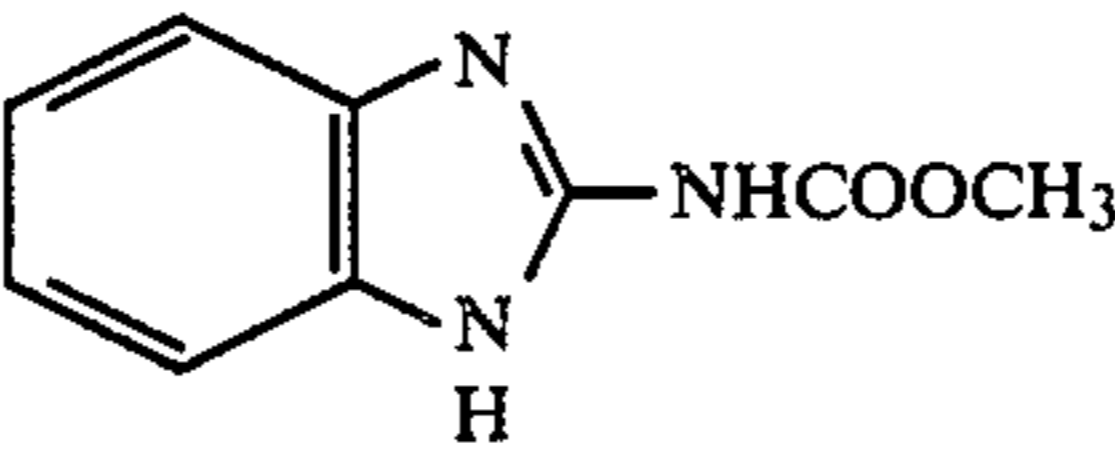
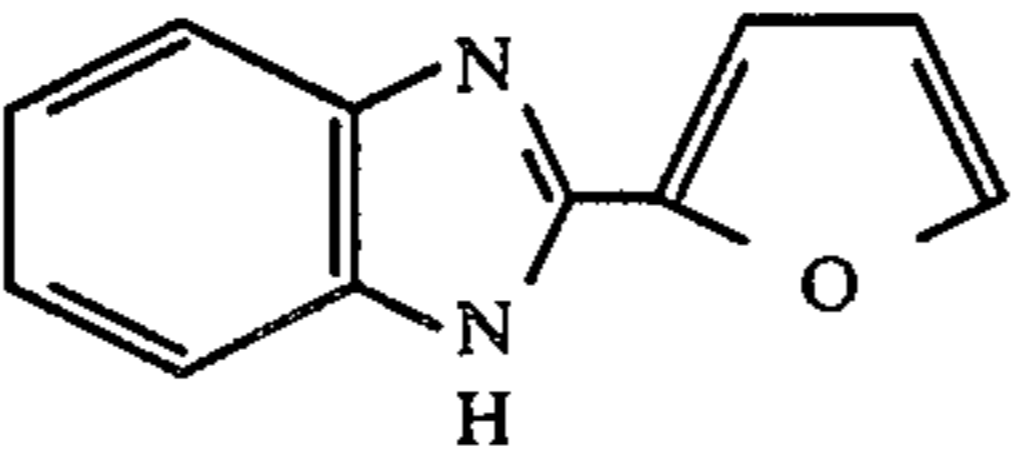
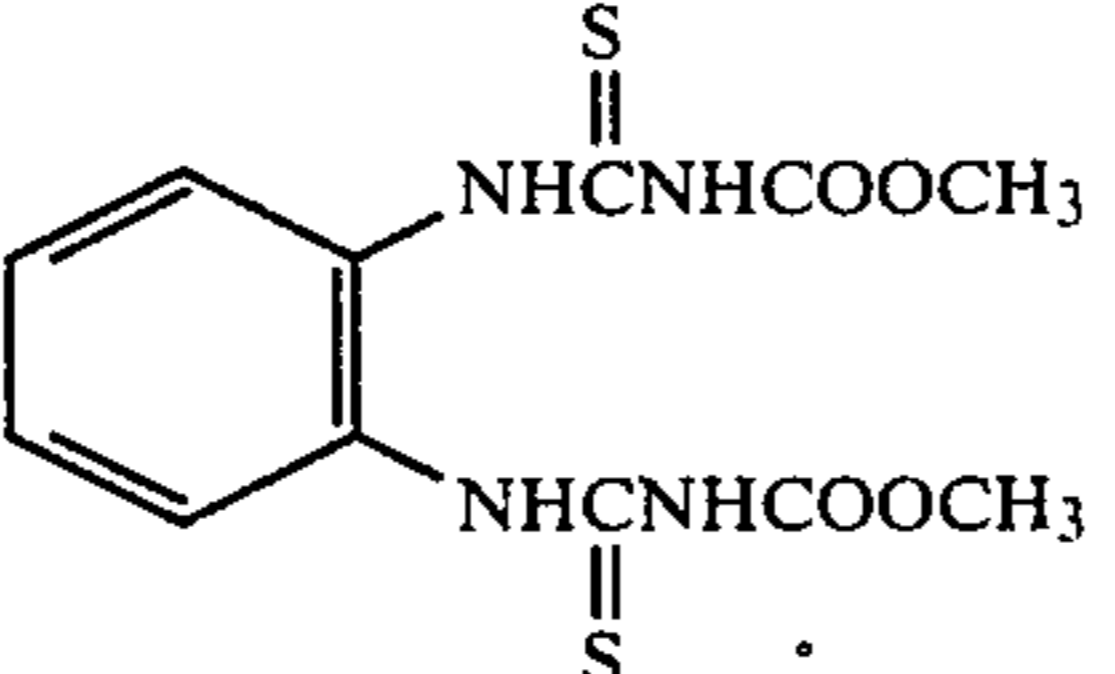
Compound	Structure	Name
A		Methyl 1-(butyl-carbamoyl)benzimidazol-2-yl-carbamate
B		2-(4-Thiazolyl)benzimidazole
C		Methyl benzimidazole-2-ylcarbamate
D		2-2(2-Furyl)benzimidazole
E		1,2-Bis(3-methoxycarbonyl-2-thioureido)benzene

TABLE 2-continued

Compound	Structure	Name
F		1,2-Bis(3-ethoxycarbonyl-2-thioureido)benzene
G		2-(O,S-Dimethyl-phosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene
H		2-(O,O-Dimethylthio-phosphorylamino)-1-(3'-methoxycarbonyl-2'-thioureido)benzene
I		N-(3',5'-Dichlorophenyl)-1,2-dimethyl-cyclopropane-1,2-dicarboximide
J		3-(3',5'-Dichlorophenyl)-1-isopropyl-carbamoylimidazolidin-2,4-dione
K		3-(3',5'-Dichlorophenyl)-5-methyl-5-vinyloxazolidin-2,4-dione
L		Ethyl (RS)-3-(3',5'-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate

Besides, the compounds of the formula (I) may be also used in admixture with other fungicides, herbicides, insecticides, miticides, fertilizers, etc.

When the compounds of the formula (I) are used as fungicides, they may be applied in such amounts as 2 to 100 grams per 10 ares. However, this amount may vary depending upon formulation forms, application times, application methods, application sites, diseases, crops and so on, and therefore, they are not limited to said particular amounts.

Some practical embodiments of the fungicidal composition according to the invention are illustratively

shown in the following Examples wherein % and part(s) are by weight.

#### FORMULATION EXAMPLE 1

Two parts of Compound No. 5, 88 parts of clay and parts of talc are thoroughly pulverized and mixed together to obtain a dust formulation containing 2% of the active ingredient.

#### FORMULATION EXAMPLE 2

Thirty parts of Compound No. 12, 45 parts of diatomaceous earth, 20 parts of white carbon, 3 parts of



sodium laurylsulfate as a wetting agent and 2 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 30% of the active ingredient.

#### FORMULATION EXAMPLE 3

Fifty parts of Compound No. 13, 45 parts of diatomaceous earth, 2.5 parts of calcium alkylbenzenesulfonate as a wetting agent and 2.5 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 50% of the active ingredient.

#### FORMULATION EXAMPLE 4

Ten parts of Compound No. 17, 80 parts of cyclohexanone and 10 parts of polyoxyethylene alkylaryl ether as an emulsifier are mixed together to obtain an emulsifiable concentrate formulation containing 10% of the active ingredient.

#### FORMULATION EXAMPLE 5

One part of Compound No. 5, 1 part of Compound No. I, 88 parts of clay and 10 parts of talc are thoroughly pulverized and mixed together to obtain a dust formulation containing 2% of the active ingredient.

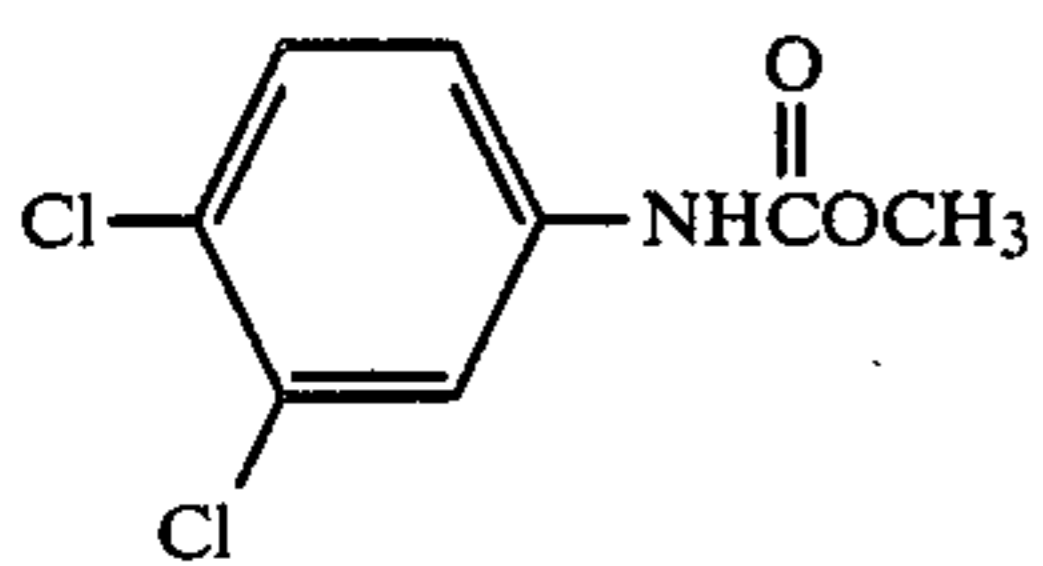
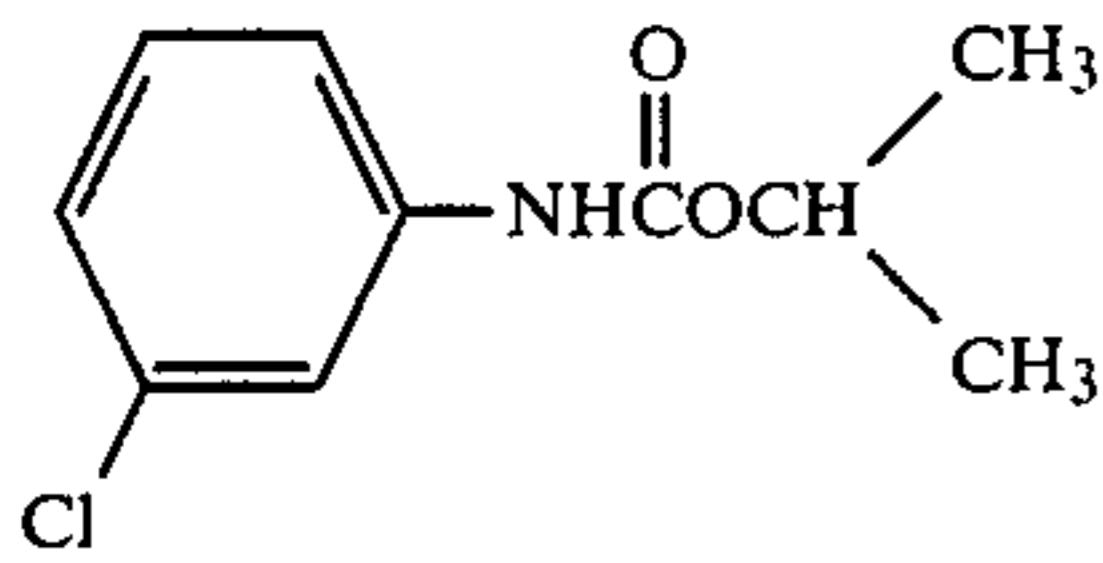
#### FORMULATION EXAMPLE 6

Twenty parts of Compound No. 3, 10 parts of Compound J, 45 parts of diatomaceous earth, 20 parts of white carbon, 3 parts of sodium laurylsulfate as a wetting agent and 2 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 30% of the active ingredient.

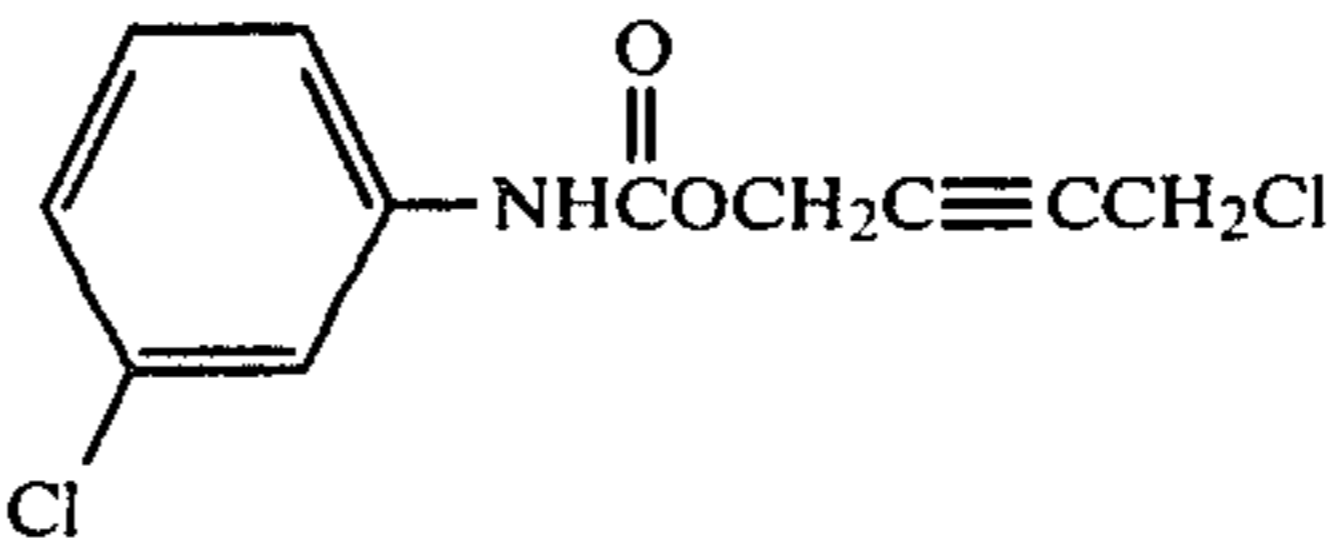
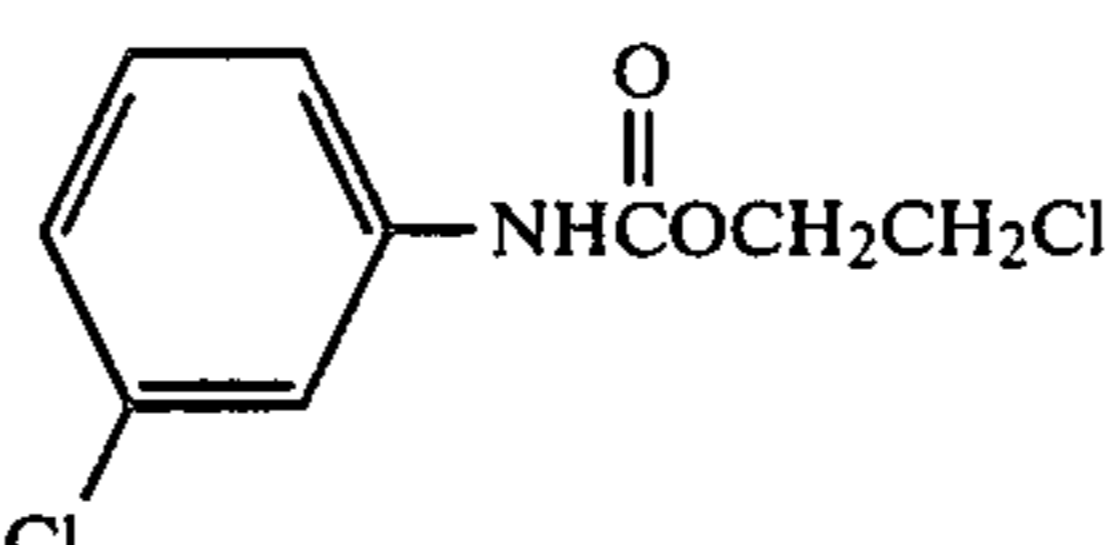
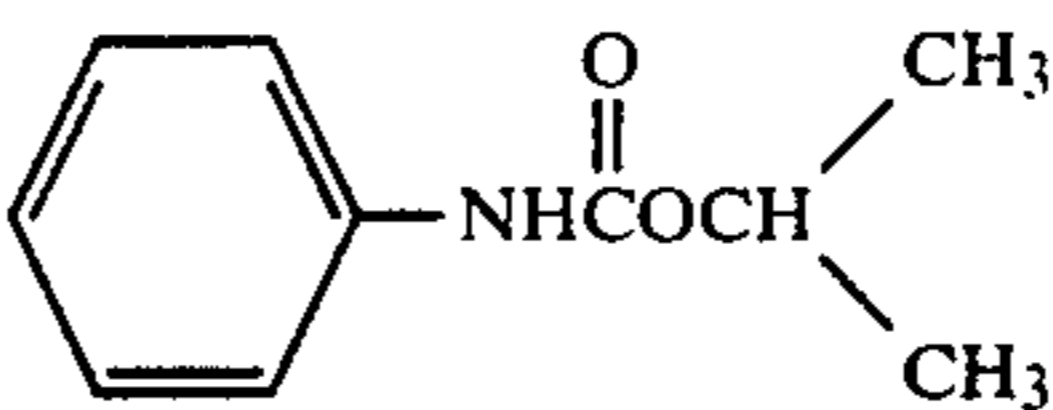
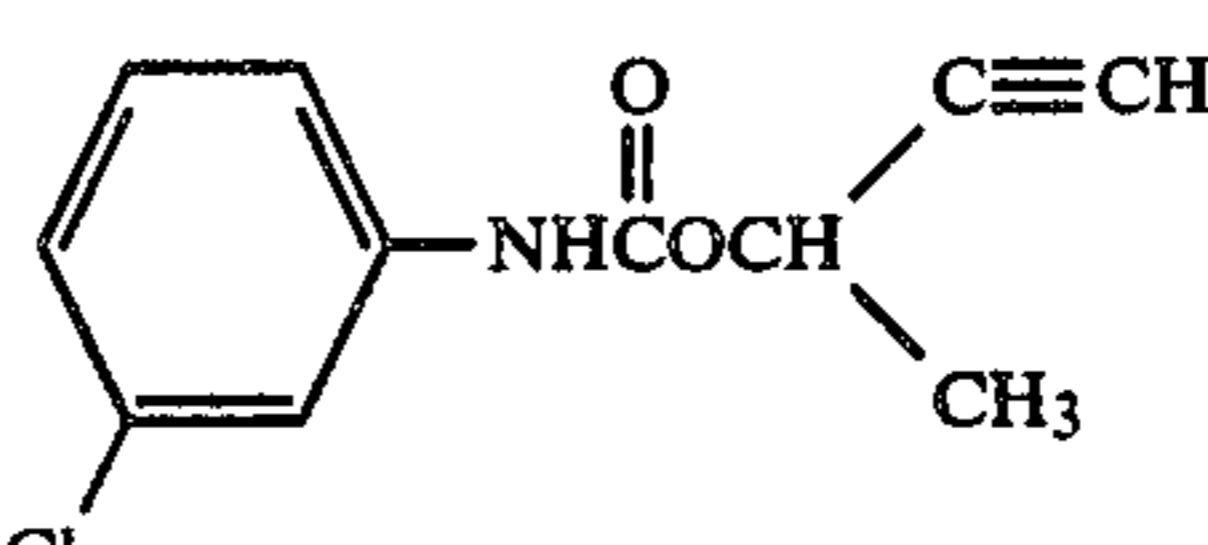
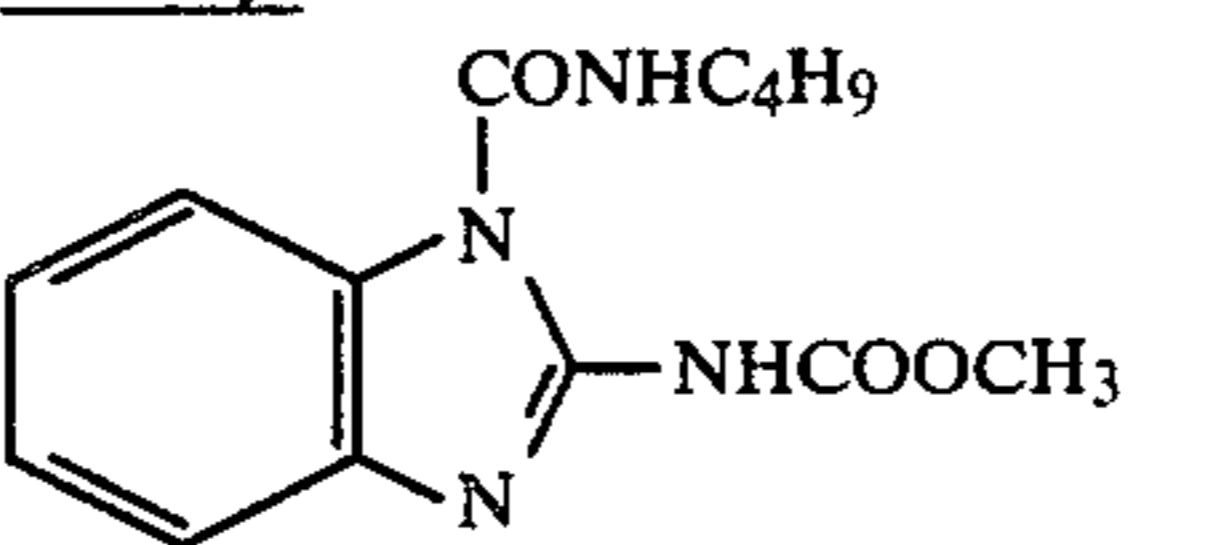
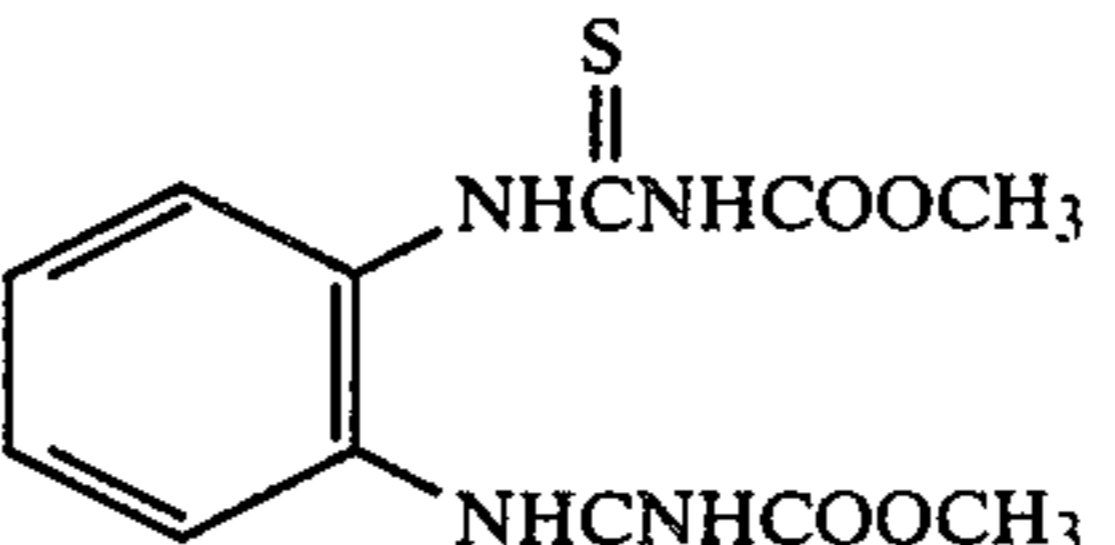
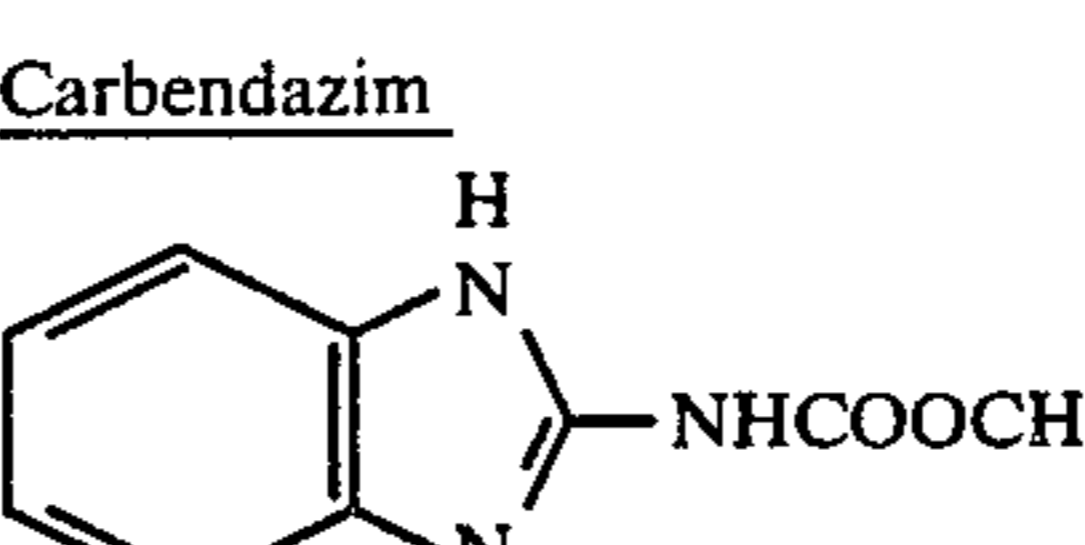
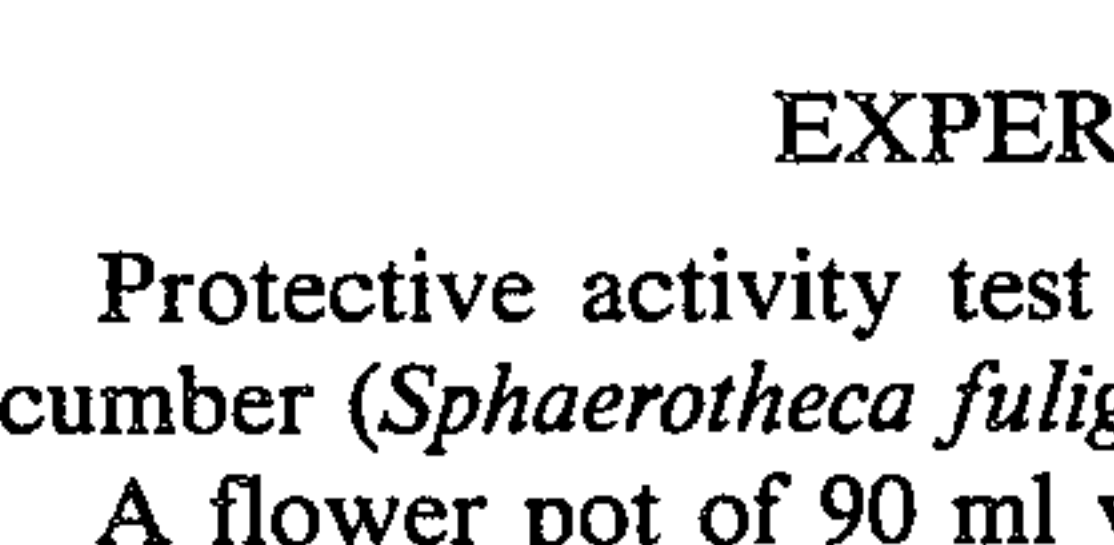
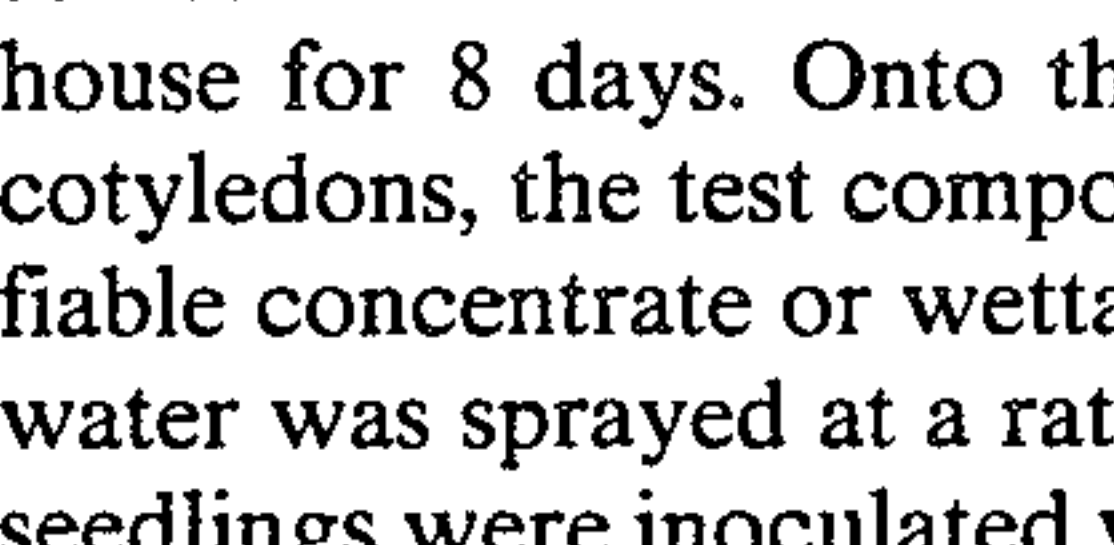
#### FORMULATION EXAMPLE 7

Ten parts of Compound No. 13, 40 parts of Compound A, 45 parts of diatomaceous earth, 2.5 parts of calcium alkylbenzenesulfonate as a wetting agent and 2.5 parts of calcium ligninsulfonate as a dispersing agent are mixed while being powdered to obtain a wettable powder formulation containing 50% of the active ingredient.

Typical test data indicating the excellent fungicidal activity of the compounds of the formula (I) are shown below. The compounds used for comparison are as follows:

Compound	Remarks
<p><u>Sweep</u></p> 	Commercially available herbicide
<p><u>Chlorpropham</u></p> 	Commercially available herbicide
<p><u>Baraban</u></p>	

-continued

Compound	Remarks
<p>5</p> 	Commercially available herbicide
<p>10</p> <p><u>CEPC</u></p> 	Commercially available herbicide
<p>15</p> <p><u>Propham</u></p> 	Commercially available herbicide
<p>20</p> <p><u>Chlorbufam</u></p> 	Commercially available herbicide
<p>25</p> 	Commercially available herbicide
<p>30</p> <p><u>Benomyl</u></p> 	Commercially available fungicide
<p>35</p> <p><u>Thiophanate-methyl</u></p> 	Commercially available fungicide
<p>40</p> 	Commercially available fungicide
<p>45</p> <p><u>Carbendazim</u></p> 	Commercially available fungicide
<p>50</p>	

#### EXPERIMENT 1

55 Protective activity test on powdery mildew of cucumber (*Sphaerotheca fuliginea*):

A flower pot of 90 ml volume was filed with sandy soil, and seeds of cucumber (var: Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days. Onto the resulting seedlings having cotyledons, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Sphaerotheca fuliginea* by spraying and further cultivated in the greenhouse. Ten days thereafter, the infectious state of the plants was observed. The degree of damage was

determined in the following manner, and the results are shown in Table 3.

The leaves examined were measured for a percentage of infected area and classified into the corresponding disease indices, 0, 0.5, 1, 2, 4:

Disease index	Percentage of infected area
0	No infection
0.5	Infected area of less than 5%
1	Infected area of less than 20%
2	Infected area of less than 50%
4	Infected area of not less than 50%

The disease severity was calculated according to the following equation:

Disease severity (%) =

$$\frac{\sum\{(\text{Disease index}) \times (\text{Number of leaves})\}}{4 \times (\text{Total number of leaves examined})} \times 100$$

The prevention value was calculated according to the following equation:

Prevention value (%) =

$$100 - \frac{(\text{Disease severity in treated plot})}{(\text{Disease severity in untreated plot})} \times 100$$

TABLE 3

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	500	100	0
3	500	100	0
4	500	100	0
5	200	100	0
12	200	100	0
13	200	100	0
Swep	200	0	0
Chlorpropham	200	0	0
Barban	200	25	0
CEPC	200	0	0
Propham	200	0	0
Chlorbufam	200	0	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Carbendazim	200	0	100

As understood from the results shown in Table 3, the compounds of the formula (I) of the invention shown an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl, Thiophanate-methyl and Carbendazim show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain. Other tested compounds structurally similar to the compounds of the formula (I) do not show any fungicidal activity on the drug-sensitive strain and the drug-resistant strain.

#### Experiment 2

Preventive effect on cercospora leaf spot of sugarbeet (*Cercospora beticola*):

A flower pot of 90 ml volume was filled with sandy soil, and seeds of sugarbeet (var: Detroit dark red) were sowed therein. Cultivation was carried out in a green-

house for 20 days. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Cercospora beticola* by spraying. The pot was covered with a polyvinyl chloride sheet to make a condition of high humidity, and cultivation was continued in the greenhouse for 10 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 4.

TABLE 4

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	500	100	0
3	500	100	0
4	500	100	0
5	200	100	0
12	200	100	0
13	200	100	0
15	200	100	0
17	200	100	0
18	200	100	0
Swep	200	0	0
Chlorpropham	200	0	0
Barban	200	34	0
CEPC	200	0	0
Propham	200	0	0
Chlorbufam	200	0	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100
Carbendazim	200	0	100

As understood from the results shown in Table 4, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl, Thiophanate-methyl and Carbendazim show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain. Other tested compounds structurally similar to the compounds of the formula (I) do not show any fungicidal activity on the drug-sensitive strain and the drug-resistant strain.

#### Experiment 3

Preventive effect on scab of pear (*Venturia nashicola*):

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of pear (var: Chojuro) were sowed therein. Cultivation was carried out in a greenhouse for 20 days. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Venturia nashicola* by spraying. The resulting plants were placed at 20° C. under a condition of high humidity for 3 days and then at 20° C. under irradiation with a fluorescent lamp for 20 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 5.

TABLE 5

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
2	500	100	0
3	500	100	0
4	500	100	0
5	200	100	0
12	200	100	0
13	200	100	0
15	200	100	0
18	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 5, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

#### Experiment 4

Preventive effect on brown leaf-spot of peanut (*Cercospora arachidicola*):

Plastic pots of 90 ml volume were filled with sandy soil, and seeds of peanut (var:Chiba hanryusei) were sowed therein. Cultivation was carried out in a greenhouse for 14 days. Onto the resulting seedling, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Cercospora arachidicola* by spraying. The resulting plants were covered with a polyvinyl chloride sheet to make a condition of humidity and cultivated in the greenhouse for 10 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 6.

TABLE 6

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
5	200	100	0
12	200	100	0
13	200	100	0
15	200	100	0
19	200	98	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 6, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

#### Experiment 5

Preventive effect on gray mold of cucumber (*Botrytis cinerea*):

Plastic pots of 90 ml volume was filled with sandy soil, and seeds of cucumber (var:Sagami-hanjiro) was sowed therein. Cultivation was carried out in a greenhouse for 8 days to obtain cucumber seedlings expanding cotyledons. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. After air-drying, the seedlings were inoculated with mycelial disks (5 mm in diameter) of the drug-resistant or drug-sensitive strain of *Botrytis cinerea* by putting them on the leaf surfaces. After the plants were infected by incubating under high humidity at 20° C. for 3 days, the rates of disease severity were observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 7.

TABLE 7

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
1	200	100	0
2	200	100	0
3	200	100	0
4	200	100	0
5	200	100	0
6	500	100	0
7	500	100	0
8	500	100	0
9	500	100	0
10	500	100	0
11	500	100	0
12	200	100	0
13	200	100	0
14	500	100	0
15	200	100	0
16	200	100	0
17	200	100	0
18	200	100	0
19	200	100	0
20	200	100	0
21	200	100	0
22	200	100	0
23	200	100	0
24	200	100	0
25	200	100	0
26	200	100	0
27	200	100	0
34	200	100	0
35	200	100	0
36	200	100	0
39	200	100	0
41	200	100	0
42	200	100	0
43	200	100	0
44	200	100	0
45	200	100	0
46	200	100	0
50	200	100	0
51	200	100	0
52	200	100	0
53	200	100	0
55	200	100	0
56	200	100	0
61	200	100	0
62	200	100	0
63	200	100	0
64	200	100	0
65	200	100	0
66	200	100	0
70	200	100	0
71	200	100	0

TABLE 7-continued

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
75	200	100	0
76	200	100	0
77	200	100	0
78	200	100	0
79	200	100	0
80	200	100	0
81	200	100	0
82	200	100	0
83	200	100	0
84	200	100	0
85	200	100	0
86	200	100	0
87	200	100	0
88	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 7, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

## Experiment 6

Preventive effect on gummy stem blight of cucumber (*Mycosphaerella melonis*):

Plastic pots of 90 ml volume were filled with sandy soil, and seeds of cucumber (var:Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days to obtain cucumber seedlings expanding cotyledons. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate or wettable powder and diluted with water was sprayed at a rate of 10 ml per pot. After air-drying, the seedlings were inoculated with mycelial disks (5 mm in diameter) of the drug-resistant or drug-sensitive strain of *Mycosphaerella melonis* by putting them on the leaf surfaces. After the plants were infected by incubating under high humidity at 25° C. for 4 days, the rates of disease severity were observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 8.

TABLE 8

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
5	200	100	0
12	200	100	0
13	200	100	0
17	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 8, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested

drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

## Experiment 7

Preventive effect on green mold of orange (*Penicillium italicum*):

Fruits of orange (var:Unshu) were washed with water and dried in the air. The fruits were immersed in a solution of the test compound prepared by diluting an emulsifiable concentrate comprising the test compound with water for 1 minute. After drying in the air, the fruits were inoculated with a spore suspension of the drug-resistant or drug-sensitive strain of *Penicillium italicum* by spraying and placed in a room of high humidity for 14 days. The degree of damage was determined in the following manner:

The fruits examined were measured for a percentage of infected area and classified into the corresponding indices, 0, 1, 2, 3, 4, 5:

Disease index	Percentage of infected area
0	No infection
1	Infected area of less than 20%
2	Infected area of less than 40%
3	Infected area of less than 60%
4	Infected area of less than 80%
5	Infected area of not less than 80%

Calculation of the degree of damage and the prevention value was made as in Experiment 1.

The results are shown in Table 9.

TABLE 9

Compound No.	Concentration of active ingredient (ppm)	Prevention value when inoculated with drug-resistant strain (%)	Prevention value when inoculated with drug-sensitive strain (%)
5	200	100	0
12	200	100	0
13	200	100	0
15	200	100	0
18	200	100	0
Benomyl	200	0	100
Thiophanate-methyl	200	0	100

As understood from the results shown in Table 9, the compounds of the formula (I) of the invention show an excellent preventive effect on the drug-resistant strain but do not show any preventive effect on the tested drug-sensitive strain. To the contrary, commercially available known fungicides such as Benomyl and Thiophanate-methyl show a notable controlling effect on the drug-sensitive strain but not on the drug-resistant strain.

## Experiment 8

Phytotoxicity on crop plants:

Plastic pots of 150 ml volume were filled with sandy soil, and seeds of wheat (var:Norin No, 61), apple (var:Kogyoku) and peanut (var:Chiba hanryusei) were sowed therein. Cultivation was carried out in a greenhouse. Onto the resulting seedlings, the test compound formulated in an emulsifiable concentrate of wettable powder and diluted with water was sprayed. After cultivation in the greenhouse for an additional 10 days,

the phytotoxicity was examined on the following criteria:

Extent	Observation
-	No abnormality
+	Abnormality due to phytotoxicity observed in a part of crop plants
++	Abnormality due to phytotoxicity observed in entire crop plants
+++	Crop plants withered due to phytotoxicity

The results are shown in Table 10

Compound No.	Concentration of active ingredient (ppm)	Phytotoxicity		
		Wheat	Apple	Peanut
5	1000	-	-	-
12	1000	-	-	-
13	1000	-	-	-
Barban	1000	-	++	++
CEPC	1000	-	++	++
Swep	1000	++	++	+

As understood from the results shown in Table 10, the compounds of the formula (I) of the invention produce no material phytotoxicity, while commercially available herbicides having a chemical structure similar thereto produce considerable phytotoxicity.

#### Experiment 9

Preventive effect on powdery mildew of cucumber (*Sphaerotheca fuliginea*):

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of cucumber (var:Sagami-hanjiro) were sowed therein. Cultivation was carried out in a greenhouse for 8 days. Onto the resulting seedlings having cotyledons, the test compound(s) formulated in an emulsifiable concentrate or wettable powder and diluted with water were sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a mixed spore suspension of the drug-resistant and drug-sensitive strain of *Sphaerotheca fuliginea* by spraying and further cultivated in the greenhouse. Ten days thereafter, the infectious state of the plants was observed. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 11.

TABLE 11

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
2	100	40
2	20	0
3	100	42
3	20	0
4	100	34
4	20	0
5	100	45
5	20	0
12	100	38
12	20	0
13	100	36
13	20	0
17	100	40
17	20	0
18	100	36
18	20	0
A	100	45
A	20	12
B	500	42

TABLE 11-continued

Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
B	100	10
C	100	42
C	20	8
D	500	36
D	100	0
E	100	44
E	20	10
F	100	43
F	20	8
G	100	42
G	20	8
H	100	40
H	20	5
2 + A	20 + 20	100
2 + B	20 + 20	100
2 + E	20 + 20	100
2 + G	20 + 20	100
3 + C	20 + 20	100
3 + D	20 + 20	100
3 + F	20 + 20	100
3 + H	20 + 20	100
4 + A	20 + 20	100
4 + D	20 + 20	100
4 + E	20 + 20	100
4 + G	20 + 20	100
5 + A	20 + 20	100
5 + B	20 + 20	100
5 + E	20 + 20	100
5 + G	20 + 20	100
12 + C	20 + 20	100
12 + D	20 + 20	100
12 + F	20 + 20	100
12 + H	20 + 20	100
13 + A	20 + 20	100
13 + D	20 + 20	100
13 + E	20 + 20	100
13 + G	20 + 20	100
17 + A	20 + 20	100
17 + B	20 + 20	100
17 + E	20 + 20	100
17 + G	20 + 20	100
18 + C	20 + 20	100
18 + D	20 + 20	100
18 + F	20 + 20	100
18 + H	20 + 20	100

As understood from the results shown in Table 11, the combined use of the compounds of the formula (I) of the invention with benzimidazole, thiophanate and/or cyclic imide fungicides show much more excellent preventive effect than their sole use.

#### Experiment 10

Preventive effect on gray mold of tomato (*Botrytis cinerea*):

A plastic pot of 90 ml volume was filled with sandy soil, and seeds of tomato (var:Fukuju No. 2) were sowed therein. Cultivation was carried out in a greenhouse for 4 weeks. Onto the resulting seedlings at the 4-leaf stage, the test compound(s) formulated in an emulsifiable concentrate or wettable powder and diluted with water were sprayed at a rate of 10 ml per pot. Then, the seedlings were inoculated with a mixed spore suspension of the drug-resistant and drug-sensitive strain of *Botrytis cinerea* by spraying and placed at 20° C. in a room of high humidity for 5 days. The degree of damage was determined in the same manner as in Experiment 1, and the results are shown in Table 12.

TABLE 12

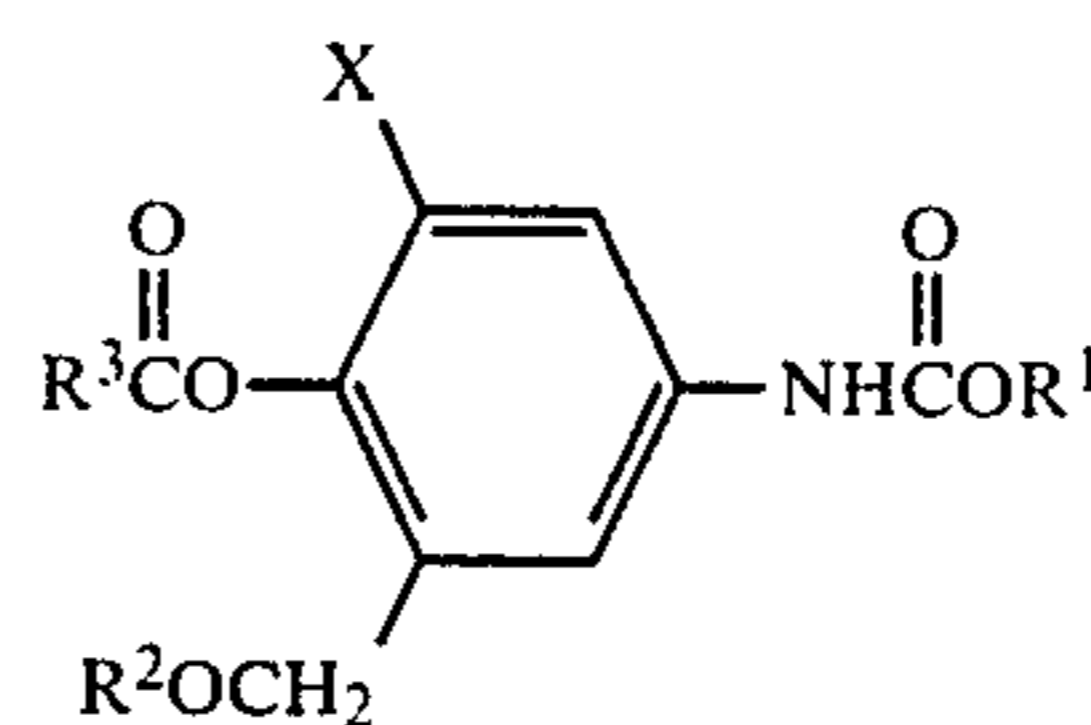
Compound No.	Concentration of active ingredient (ppm)	Prevention value (%)
2	100	32
2	20	0
3	100	44
3	20	0
4	100	44
4	20	0
5	100	38
5	20	0
12	100	40
12	20	0
13	100	42
13	20	0
15	100	43
15	20	0
I	100	48
I	20	22
J	500	46
J	100	18
K	100	42
K	20	15
L	500	42
L	100	12
2 + I	20 + 50	100
2 + J	20 + 50	100
3 + I	20 + 50	100
3 + K	20 + 50	100
4 + I	20 + 50	100
4 + J	20 + 50	100
4 + K	20 + 50	100
4 + L	20 + 50	100
5 + I	20 + 50	100
5 + J	20 + 50	100
12 + I	20 + 50	100
12 + K	20 + 50	100
13 + I	20 + 50	100
13 + J	20 + 50	100
13 + K	20 + 50	100
13 + L	20 + 50	100
15 + I	20 + 50	100
15 + J	20 + 50	100

As understood from the results shown in Table 12, the combined use of the compounds of the formula (I) 40

of the invention with benzimidazole, thiophanate and/or cyclic imide fungicides show much more excellent preventive effect than their sole use.

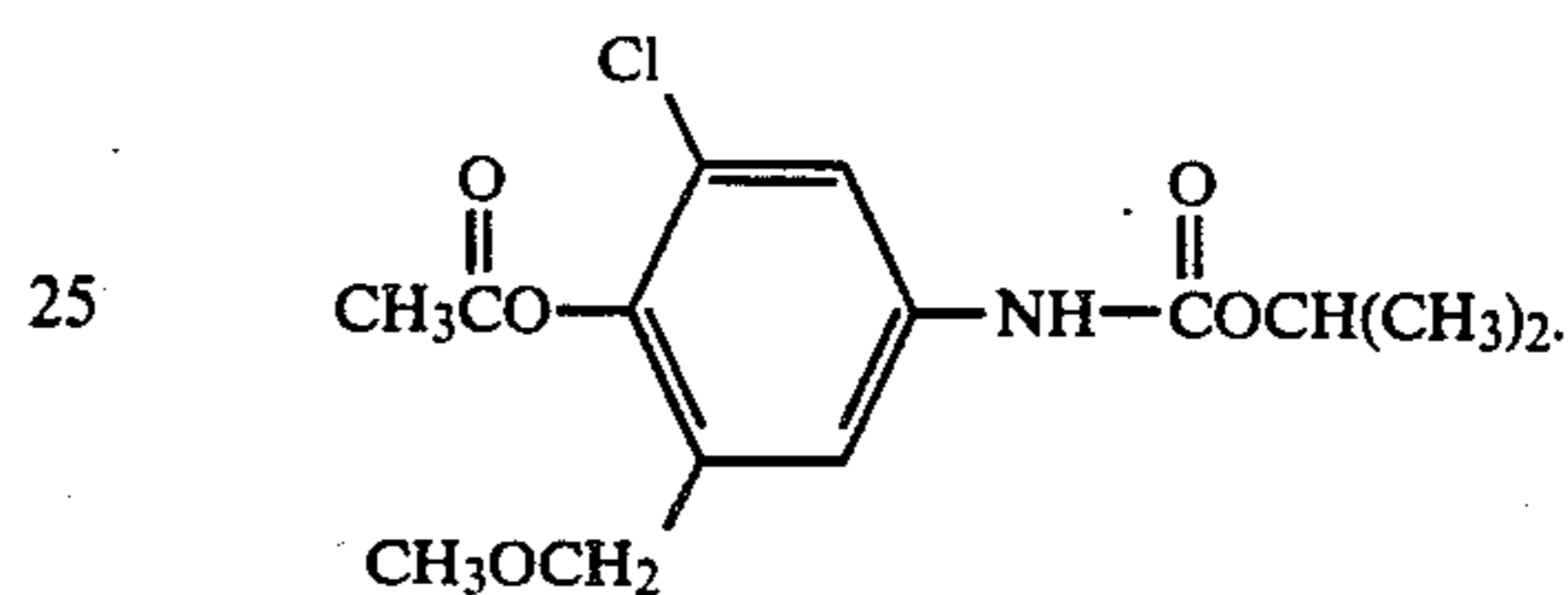
What is claimed is:

1. A compound of the formula:



15 wherein X is a halogen atom; R<sup>1</sup> is a lower alkyl group, a lower alkenyl group, a lower alkynyl group, a halo (lower) alkyl group or a lower alkoxy (lower) alkyl group; R<sup>2</sup> and R<sup>3</sup> are both a lower alkyl group.

2. The composition of claim 1, wherein the active ingredient is a compound represented by the formula:



30 3. A fungicidal composition which comprises as an essential active ingredient a fungicidally effective amount of a compound according to claim 1, and an inert carrier or diluent.

4. A method for controlling plant pathogenic fungi which comprises applying a fungicidally effective amount of at least one compound according to claim 1 to plant pathogenic fungi.

5. The method according to claim 4, wherein the plant pathogenic fungi is the drug-resistant strain.

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